Electronic Spectra of 1-Substituted and 1,4-Disubstituted 1,3-Butadienes. Comparisons between Geometric Isomers[1]

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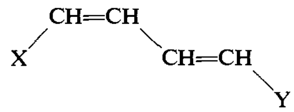
Abstract: The ultraviolet absorption spectra of the cis–trans isomers of a variety of 1-substituted and 1,4-disubstituted 1,3-butadienes have been measured in the 200–300-nm region in the vapor phase. Each isomer shows a single intense band, which is assignable to the lowest singlet $\pi \rightarrow \pi^*$ transition. With all the diene derivatives, which are considered to be predominantly in the planar s-trans conformation, both the energy and oscillator strength of the transition are found to be greater for trans isomers than for the corresponding cis isomers. These qualitative features of spectra are wholly justifiable from the results of the routine semiempirical SCF–MO computations of the Pariser–Parr–Pople type. It is pointed out that, within the theoretical framework based on the virtual orbital approximation, the electronic effect of geometric structure on the excitation energy is reflected most conspicuously in the molecular Coulomb repulsion integral between the highest occupied and lowest vacant π orbitals. As a corollary, it is predicted that the lowest triplet excitation energy should also be greater for trans isomers, in agreement with limited experimental data.

The electronic spectra of organic compounds are known to be largely dependent on the stereostructure as well as chemical constitution of the chromophores involved. Apparently, however, little consideration has ever been given to the precise effects of geometric isomerism on the spectra of olefinic compounds. One familiar example is the case of *cis*- and *trans*-stilbenes, in which the former isomer shows absorption peaks in shorter wavelength regions as compared with the latter.[2] This fact has been attributed to the nonplanarity (the twisting around the single bonds) of the cis isomer due to the *steric repulsion* between the two phenyl groups located cis to each other.[3,4] Both the simple LCAO–MO treatments[3,5] and the LCAO–SCF–CI computations[6,7] rationalize the interpretation.

The problem with which we are going to be primarily concerned here is the effects of geometric structure in the absence of steric effects. Beveridge and Jaffé[6] have demonstrated theoretically that the lowest singlet excitation energy for *cis*-stilbene in solution would be lower than that for *trans*-stilbene, if the former isomer existed in a planar conformation as in the case of the latter. Cases like this are indeed met with in the spectra of butadiene derivatives. Thus, Viehe[8] reported that in the gaseous phase *trans*-1-fluoro-1,3-butadiene shows an absorption peak at 215 nm, while its cis isomer has the corresponding peak at 220 nm, the $\pi \rightarrow \pi^*$ excitation energy being greater for the trans isomer by 0.13 eV. He further gave comparative gas-spectral data for the three geometric isomers of 1,4-difluoro- as well as 1,4-dichloro-1,3-butadiene, for which the excitation energies decrease in the order: trans,trans > trans,cis > cis,cis.[9] All these dienes are considered to be planar in structure, as may be deduced from the observation of the long-range pmr couplings between the hydrogen atoms which are attached to the 1- and 4-carbon atoms.[10,11]

Most likely, Viehe's spectral data are a reflection of some *electronic effect* of the fully conjugated chromophores. We have felt this point to deserve extensive investigation, particularly in view of the broad usefulness of the ultraviolet spectroscopy in structural determination of unsaturated compounds.

We have thus undertaken, in the present work, to compare systematically the gas-phase spectra for geometric isomers of a variety of 1-substituted and 1,4-disubstituted 1,3-butadienes. These types of compounds



X = CH_3, F, Cl, OC_2H_5, $OCOCH_3$, $COCH_3$, $COOCH_3$, CN, or $CH{=}CH_2$

$Y = \begin{cases} H & (1\text{-substituted}) \\ X' & (1,4\text{-disubstituted}) \end{cases}$

are not only likely to be planar in structure (predominantly in the s-trans conformation[10,11]), but their spectral features are relatively simple. It has been verified that, aside from some exceptional cases, in which coplanarity is not to be expected for cis isomers, both excitation energy and extinction coefficient are generally greater for the trans configuration, irrespective of the sort of the terminal substituents. The generalization is found to be justifiable from the usual π-electron theory of the Pariser–Parr–Pople (PPP) type.[12,13] These results lend support to and extend the aforementioned theoretical demonstration of Beveridge and Jaffé.[6]

Experimental Section

The 1-ethoxybutadiene (**2**)[14,15] and methyl butadiene-1-carboxylate (**5**)[16] were prepared according to the methods given in the

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[1] Taken in part from a doctorate thesis to be submitted by K. Yamaguchi to the Osaka University.

[2] H. Suzuki, *Bull. Chem. Soc. Jap.*, **33**, 381 (1960).

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

[4] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, pp 424–434.

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

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

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

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

[9] H.-G. Viehe and E. Franchimont, *ibid.*, **97**, 602 (1964).

[10] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, **87**, 3451 (1965).

[11] A. A. Bothner-By and D. Jung, *ibid.*, **90**, 2342 (1968).

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

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

[14] A. E. Montagna and D. H. Hirsh, U. S. Patent, 2,905,722 (1959).

literature. 1-Cyanobutadiene (**6**) and sorbonitrile (1-cyano-1,3-pentadiene, **13**) were synthesized by the condensation of the appropriate aldehydes with cyanoacetic acid, followed by decarboxylation.[17] Crotonylidene acetone (methyl 1,3-pentadienyl ketone, **12**) was synthesized by the condensation between crotonaldehyde and acetone.[18] All these compounds were the mixtures of geometric isomers. 1,3-Pentadiene (**1**) and 2,4-hexadiene (**8**) were purchased and distilled. Both these dienes, being almost exclusively trans and trans,trans in configuration, were irradiated with a mercury lamp for several hours to effect partial geometric isomerization.

The various conjugated dienes were then separated into isomers by means of preparative gas chromatography. Column packings used were Apiezon Grease L for **2**, poly(ethylene glycol) for **5**, **6**, **12**, and **13**, and $AgNO_3$-containing ethylene glycol for **1** and **8**. Column length (5–10 m) and operating temperature (80–190°) were so chosen as to best suit the separation. Hydrogen was used as carrier gas at a flow rate of 25 ml/min. Each sample was injected by *ca.* 50 μl at a time.

All the geometric isomers were identified as such from the magnitude of the nmr coupling constants observed between the relevant ethylenic hydrogen atoms. Gas chromatography showed that all samples had an isomeric purity exceeding 95%, except for *trans,cis*-**13**, which was only 76% pure and was contaminated with its cis,cis (10%), cis,trans (9%), and trans,trans (5%) isomers.

The absorption spectra were recorded on a Cary Model 15 spectrophotometer at room temperature. Sample solutions were prepared by dissolving *ca.* 20 mg of diene in 10 cc of *n*-hexane. One drop of each sample solution was completely evaporated in a quartz cell of a 10-cm length and was subjected to the vapor spectra measurement. The wavelength readings were accurate to within ±0.5 nm. Evaluations of the extinction coefficients were not practiced for the vapor spectra, but it was confirmed that the relative absorbances of isomers were essentially equal to those obtained for the solution spectra.

For measurements in solution, the sample solutions were further diluted to *ca.* 10^{-5} *M*. A quartz cell of a 1-cm path length was used. *n*-Hexane used as solvent was purified by passing it through an aluminum column of 1.5 m in length and 2 cm in diameter. The extinction coefficients observed were not corrected for isomeric impurity.

Method of Calculations

The LCAO-MO-CI method of the Pariser–Parr–Pople type was used in order to calculate the energies and oscillator strengths of the $\pi \rightarrow \pi^*$ transitions. The integral parameters necessary for the calculations are the atomic core integrals, H_{rr} and H_{rs}, and the electronic repulsion integrals, $(rr|rr)$ and $(rr|ss)$. Penetration integrals have been neglected throughout this work.

The diagonal core integrals, H_{rr}, are expressed usually as[12,13]

$$H_{rr} = -I_r - \sum_{r \neq s} n_s(rr|ss) \qquad (1)$$

where I_r is the valence-state ionization potential of atom r and where n_s is the charge on the atomic core s. The values of I_r have been obtained from the tables of data compiled by Hinze and Jaffé[19] and by Moore.[20] When atom r contributes two π electrons to conjugation, the second ionization potential was chosen as I_r. The quantity n_s is either 1 or 2, depending on whether atom s contributes one or two π electrons to conjugation.

The off-diagonal core resonance integrals, H_{rs}, between two neighboring atoms r and s are evaluated in this work according to the Wolfsberg–Helmholtz formula[21]

$$H_{rs} = -(\kappa/2)S_{rs}(I_r + I_s) \qquad (2)$$

where S_{rs} is the overlap integral between the Slater pπ atomic orbitals on atoms r and s. The parameter κ is empirically assigned a value of unity.

The one-center electron repulsion integrals $(rr|rr)$ are evaluated from the Pariser approximation[22]

$$(rr|rr) = I_r - E_r \qquad (3)$$

where E_r is the valence-state electron affinity[19,20] of atom (n_r = 1) or cationic core (n_r = 2). The two-center repulsion integrals $(rr|ss)$ are estimated according to the Nishimoto–Mataga formula.[23]

The numerical values of I_r and $(rr|rr)$ used in this investigation are listed in Table I. The hyperconjugative model was assumed for the methyl group.[24]

Table I. Integral Parameters, eV

Atom	n_r	Valence state	I_r[a]	$(rr\|rr)$
C(double)	1	tttπ	11.16	11.13
C(triple)	1	dd$\pi\pi$	11.19	11.09
N(cyano)	1	d^{2}d$\pi\pi$	14.18	12.52
N(amino)	2	tttπ^2	28.71	16.75
O(carbonyl)	1	d^{2}d$\pi^2\pi$	17.91	15.20
O(ether)	2	t^{2}ttπ^2	34.08	18.78
F	2	s^{2}p$\pi^2\pi^2$	34.98[b]	17.56
Cl	2	s^{2}p$\pi^2\pi^2$	23.80[b]	10.83
H_3(methyl)	1	p	10.26[c]	9.33[c]

[a] Reference 19, unless otherwise noted. [b] Reference 20; promotion energies are neglected. [c] Reference 24.

The spin configurations are constructed using the SCF closed-shell and virtual orbitals. Twenty iterations were sufficient to obtain convergence to 0.001 in these orbital energies. The configuration interactions were treated by including lower 10 (at maximum) singly excited configurations. The energies and moments of transitions were obtained from the final wave functions and states.

We assume all the butadiene derivatives to be in the s-trans conformation with respect to the 2–3 single bond, unless otherwise noted. We further assume that molecular geometry of each 1-substituted butadiene may be constructed schematically by replacing one vinyl group of the parent butadiene with a substituted vinyl group XCH=CH–. The distance and angles associated with the 2–3 bond were kept unaltered from those of butadiene. 1,4-Disubstituted derivatives may likewise be constructed from two such groups. The geometries of butadiene and substituted vinyl groups were taken from the literature.[25] The structural difference between geometric isomers of a given butadiene derivative was thus reduced simply to a matter for the alternate choice between the two possible ways of local

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(15) T. Fueno, T. Tsunetsugu, K. Arimoto, and J. Furukawa, *J. Polym. Sci., Part A-1*, **9**, 163 (1971).

(16) E. P. Kohler and F. R. Butler, *J. Amer. Chem. Soc.*, **48**, 1041 (1926).

(17) W. Borshe and R. Manteuffel, *Justus Liebigs Ann. Chem.*, **512**, 108 (1934).

(18) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1103 (1952).

(19) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962); *J. Phys. Chem.*, **67**, 1501 (1963).

(20) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular No. 467, Vol. 1, Washington, D. C., 1949.

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

(22) R. Pariser, *ibid.*, **21**, 568 (1953).

(23) K. Nishimoto and N. Mataga, *Z. Phys. Chem. (Frankfurt am Main)*, **12**, 335 (1957).

(24) T. Morita, *Bull. Chem. Soc. Jap.*, **33**, 1486 (1960).

(25) A. D. Mitchell, Ed., "Table of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

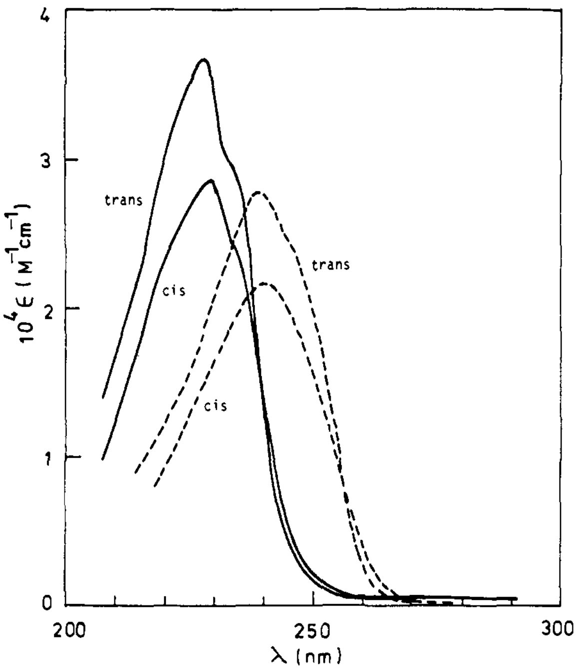


Figure 1. Ultraviolet absorption spectra of *cis*- and *trans*-1-cyanobutadienes (**6**) in the vapor phase (—) and in *n*-hexane solution (---). The extinction coefficients of the vapor spectra are correct only relatively to each other isomer.

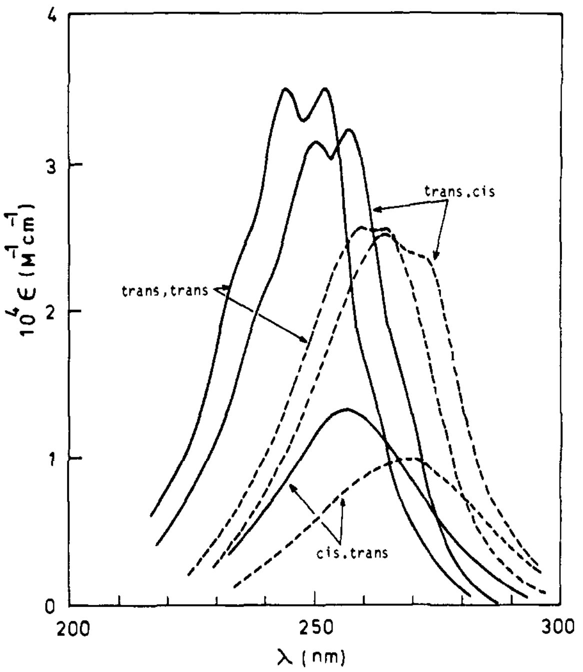


Figure 2. Ultraviolet absorption spectra of *cis,trans*-, *trans,cis*-, and *trans,trans*-crotonylidene acetone (**12**) in the vapor phase (—) and in *n*-hexane solution (---). The extinction coefficients of the vapor spectra are correct only relatively to each other isomer.

placement for each substituent. In the present treatment, therefore, any effect of geometric isomerism on the electronic states of dienes will be interpreted as arising only from the differences in some of the long-range two-center electron repulsion integrals associated with the substituents. All computations were performed on the KDC-II at the Computation Center of Kyoto University.

Results and Discussion

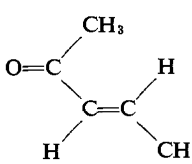
A. General Features of the Observed Spectra. Figure 1 shows the absorption spectra of the cis and trans isomers of 1-cyanobutadiene (**6**), as an example, both in the gaseous state and in *n*-hexane solution. In either phase, the observed spectra have one intense band maximum in the wavelength range between 200 and 300 nm. These absorption maxima may be used for our present purposes.

The spectral data obtained for various butadiene derivatives in this work are summarized in Table II, together with some pertinent data reported by other investigators.[8,9,26,27] No doubt, these data all correspond to the lowest $\pi \rightarrow \pi^*$ excitation.

Inspection of the experimental data given in Table II indicates that, with most of the derivatives studied, both the energy, Δ^1E, and extinction coefficient, ϵ, of the lowest excitation are more or less greater for the isomer(s) which structurally has more of the trans ethylenic moieties. This is true, irrespective of the polarity character of the substituents, electron donating or electron attracting. The general trend observed has no direct bearing with the relative stabilities of geometric isomers; the halogeno derivatives (**4**, **9**, and **10**) have been claimed to be more stable in the cis configuration,[8,9] whereas pentadiene (**1**)[28] and 1-ethoxybutadiene (**2**)[29] have been established to be thermochemically trans stable by *ca.* 1 kcal/mol at ordinary temperature.

The only exceptions to the above generalization are hexatriene (**7**) and methyl muconate (**11**); *cis*-**7** and *cis,cis*-**11** have greater values of Δ^1E than *trans*-**7** and *cis,trans*-**11**, respectively. The anomaly encountered in **7** is apparently because of the twisting of the *cis*-triene framework around its single bonds.[27,30] On the other hand, the irregularity of Δ^1E for the isomers of **11** is perhaps a result of complicating solvent effects. Since **11** is the only compound that lacks vapor spectral data, gas-phase studies are greatly required for it.

Vapor spectra observed for crotonylidene acetone (**12**) are somewhat unusual and hence will deserve special mention. In the 200–300-nm region, both the trans,-trans and trans,cis isomers showed two strong transitions which are separated by *ca.* 8 nm and are almost of equal intensity (see Figure 2). The presence of two strong bands can hardly be ascribable to coexistence of conformers.[31] Probably, it is because of either two strong $\pi \rightarrow \pi^{*32}$ or vibrational transitions of the all-s-trans conformers. Although we cannot decide which



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(26) K. K. Georgieff and A. Dupre, *Can. J. Chem.*, **38**, 1071 (1960).

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

(28) K. W. Egger and S. W. Benson, *ibid.*, **87**, 3311 (1965).

(29) T. Okuyama, T. Fueno, and J. Furukawa, *Tetrahedron*, **25**, 5409 (1969).

(30) R. S. Becker, K. Inuzuka, and D. E. Balke, *J. Amer. Chem. Soc.*, **93**, 38 (1971).

(31) Although two stable planar conformations are conceivable for the acetoxyl group involved, it is most likely that the s-trans conformation is the far more favorable in both these isomers, as has been confirmed to be the case with *trans*-propenyl methyl ketone [Y. Kobuke, T. Fueno, and J. Furukawa, *ibid.*, **92**, 6548 (1970)].

(32) N. L. Allinger, T. W. Stuart, and J. C. Tai, *ibid.*, **90**, 2809 (1968).

Table II. Lowest Singlet $\pi \rightarrow \pi^*$ Transitions of Terminal-Substituted 1,3-Butadienes

Serial no.	Substituents		Geometry[a]	Obsd[b]			Calcd			
	X	Y		Δ^1E, eV	λ_{max}, nm	$10^{-4}\epsilon$, M^{-1} cm^{-1}	Δ^1E, eV	J_{hl}, eV	f_x	f_y
			1-Substituted Butadienes							
1	CH_3	H	Cis	5.77	215 (225)		5.881	5.525	1.157	0.000
			Trans	5.81	213 (221)		5.910	5.491	1.169	0.160
2	OC_2H_5	H	Cis	5.25	236 (248)	(1.76)	6.081	5.897	1.036	0.025
			Trans	5.50	225 (236)	(1.90)	6.106	5.882	1.053	0.074
3	$OCOCH_3$	H	Cis	5.30	234[c]	2.6[c]	5.729	5.586	0.779	0.016
			Trans	5.32	233[c]	2.6[c]	5.730	5.436	0.762	0.015
4	F	H	Cis	5.64	220[d]	0.95[d]	6.294	6.010	1.040	0.031
			Trans	5.77	215[d]	1.0[d]	6.313	5.997	1.054	0.065
5	$COOCH_3$	H	Cis	5.30	234 (245)	(1.65)	5.400	5.342	1.215	0.000
			Trans	5.37	231 (242)	(1.81)	5.419	5.268	1.229	0.119
6	CN	H	Cis	5.42	229 (240)	(2.18)	5.477	5.312	1.084	0.012
			Trans	5.44	228 (239)	(2.80)	5.534	5.257	1.114	0.228
7	$CH{=}CH_2$	H	Cis	5.17	240[e]	4.1[e]	5.351	5.147	1.393	0.000
			Trans	5.15	241[e]	4.8[e]	5.383	5.107	1.408	0.113
			1,4-Disubstituted Butadienes							
8	CH_3	CH_3	Cis,cis	5.64	220 (230)	(~2.0)	5.487	5.143	1.297	0.015
			Cis,trans	5.70	218 (228)	(2.28)	5.502	5.117	1.306	0.032
			Trans,trans	5.73	216 (226)	(2.70)	5.530	5.083	1.318	0.241
9	F	F	Cis,cis	5.69	218[f]		6.206	5.983	1.093	0.019
			Cis,trans	5.82	213[f]		6.214	5.969	1.097	0.044
			Trans,trans	5.85	212[f]		6.223	5.954	1.103	0.081
10	Cl	Cl	Cis,cis	5.04	246[f]	2.61[f]	5.788	5.523	1.115	0.002
			Cis,trans	5.10	243[f]	2.86[f]	5.804	5.506	1.120	0.040
			Trans,trans	5.16	240[f]	3.25[f]	5.822	5.483	1.128	0.129
11	$COOCH_3$	$COOCH_3$	Cis,cis	(4.79)[g]	(259)[g]	(2.64)[g]	4.840	4.911	1.507	0.002
			Cis,trans	(4.77)[g]	(260)[g]	(2.98)[g]	4.851	4.872	1.504	0.036
			Trans,trans	(4.79)[g]	(259)[g]	(3.67)[g]	4.890	4.839	1.509	0.173
12	$COCH_3$	CH_3	Cis,cis				4.772	4.789	1.097	0.019
			Cis,trans	4.83	256 (269)	(0.97)	4.775	4.769	1.090	0.005
			Trans,cis	4.82	257 (272)	(2.37)	4.812	4.708	1.139	0.064
			Trans,trans	4.92	252 (264)	(2.57)	4.835	4.667	1.147	0.227
13	CN	CH_3	Cis,cis	5.17	240 (253)	(2.36)	5.137	4.969	1.225	0.035
			Cis,trans	5.25	236 (248)	(2.56)	5.143	4.944	1.230	0.004
			Trans,cis	5.19	239 (252)	(2.69)	5.171	4.922	1.254	0.084
			Trans,trans	5.28	235 (248)	(3.07)	5.200	4.886	1.265	0.310

[a] The geometry notations for the 1,4-disubstituted butadienes refer first to the placement of X and then to Y. [b] The data given in parentheses are those obtained in solution. Solvent is *n*-hexane, unless otherwise specified. [c] Reference 26. [d] Reference 8. [e] Reference 27. [f] Reference 9. [g] Measured in ethanol: J. A. Elvidge, R. P. Linstead, P. Sins, and B. A. Orkin, *J. Chem. Soc.*, 2235 (1950).

Table III. Excited Singlet States of *cis*- and *trans*-1-Cyanobutadienes[a]

Geometry	State (i)	Δ^1E, eV	f_x	f_y	$^1\Psi_i$[b]		
					$A_{h.l}$	$A_{h-1.l}$	$A_{h.l+1}$
Cis	1	5.477	1.084	0.012	0.992	−0.048	0.098
		(5.523)	(1.173)	(0.008)			
	2	7.072	0.067	0.000	0.102	0.702	−0.684
	3	7.924	0.019	0.271	−0.043	0.641	0.687
Trans	1	5.534	1.114	0.228	0.994	−0.032	0.077
		(5.576)	(1.176)	(0.208)			
	2	7.185	0.050	0.003	0.078	0.699	−0.678
	3	7.944	0.017	0.059	−0.040	0.631	0.694

[a] The entries given in parentheses are the values before configuration interaction treatments. [b] The state functions are expressed as $^1\Psi_i = \Sigma_{j\neq k}A_{j.k}{}^1\Phi_{j.k}$.

of these latter two possibilities is the more likely, it is out of question that the transitions corresponding to the longer wavelength bands should be the ones to be considered in the present context. The experimental data listed in Table II are those for such lower transitions.

B. Excitation Energies. Table III gives the excitation energies, Δ^1E, oscillator strengths, f_x and f_y, and wave functions, $^1\Psi_i$, computed for lower excited singlet states of *cis*- and *trans*-1-cyanobutadienes (6). The spin configuration $^1\Phi_{h,l}$ corresponds to a one-electron singlet transition from the highest occupied molecular orbital ψ_h to the lowest vacant molecular orbital ψ_l. The molecular orbitals ψ_{h-1} and ψ_{l+1} respectively denote the next highest occupied and lowest levels. The LCAO functions and energies of these orbitals are given in Table IV. The coordinate axes and atomic orbital numberings used are as illustrated in Figure 3.

The energies calculated for the lowest excited states (cis, 5.477 eV; trans, 5.534 eV) are in reasonable agreement with the observed (cis, 5.42 eV; trans, 5.44 eV). The state functions $^1\Psi_1$ indicate that for either isomer the lowest excited state is well represented by a single spin configuration $^1\Phi_{h,l}$, which intrinsically corresponds to allowed transition. Configuration interactions lower

Table IV. SCF Molecular Orbitals of *cis*- and *trans*-1-Cyanobutadienes

		$\psi_j{}^a$						
Geometry	j	C_{j1}	C_{j2}	C_{j3}	C_{j4}	C_{j5}	C_{j6}	E_j, eV
Cis	6	−0.5248	0.4679	−0.3370	0.2170	0.4967	−0.3153	2.193
	5	0.0922	0.2361	−0.5619	0.4930	−0.4795	0.3834	0.555
	4 (*l*)	−0.4573	0.4949	0.2633	−0.4675	−0.3146	0.3988	−1.943
	3 (*h*)	0.5281	0.4223	−0.3661	−0.5233	−0.0852	−0.3574	−10.143
	2	0.1758	0.4315	0.5727	0.4517	−0.2882	−0.4098	−12.633
	1	0.4441	0.3406	0.1983	0.1160	0.5779	0.5477	−14.359
Trans	6	−0.5255	0.4677	−0.3348	0.2138	0.4985	−0.3144	2.189
	5	0.0885	0.2393	−0.5614	0.4939	−0.4779	0.3840	0.547
	4 (*l*)	−0.4573	0.4936	0.2665	−0.4679	−0.3146	0.3978	−1.953
	3 (*h*)	0.5285	0.4244	−0.3646	−0.5216	−0.0877	−0.3576	−10.145
	2	0.1736	0.4288	0.5734	0.4537	−0.2878	−0.4105	−12.648
	1	0.4443	0.3412	0.1999	0.1161	0.5777	0.5469	−14.361

[a] The molecular orbitals are expressed as $\psi_j = \Sigma_r C_{jr}\chi_r$.

both the energy and oscillator strength ($f_x + f_y$) only slightly. The second and third lowest excited states are calculated to be 1.5–2.0 eV higher lying than the first, and hence are not expected to be observable under our experimental conditions. Transition to neither of these high-energy states can be adequately described as one-electron excitation between any two specific molecular orbitals. The corresponding oscillator strengths are small as compared with the strength of the lowest $\pi \rightarrow \pi^*$ transition.

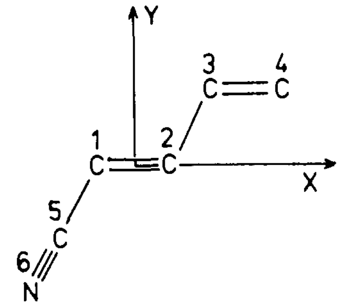


Figure 3. Coordinate systems and atomic orbital numberings of *trans*-1-cyanobutadiene. The coordinates for the cis isomer remain the same, except for the y ordinates of the 5 and 6 atomic orbitals.

Analogous calculations have been performed for all the remaining compounds. For any isomer of these compounds including **12**, the lowest $\pi \rightarrow \pi^*$ excitation was the only intense transition in the wavelength range of our interest. In what follows, we will be concerned only with this lowest $\pi \rightarrow \pi^*$ transition. The calculated values of Δ^1E, f_x, and f_y are given in Table II.

It may be noticed in Table II that the Δ^1E values calculated for trans isomers are greater than those for the corresponding cis isomers, with no exceptional case whatsoever. The differences between the calculated values are a few hundredths of an electron volt, in rough agreement with those found experimentally.

At this point, we would like to make one comment on the calculated energies. As may be seen in Table II, numerical agreements between theory and experiment are not excellent for all the compounds investigated. This inaccuracy of the theoretical results is largely because of (1) the use of the virtual orbital approximation and (2) the poorness of the valence-orbital basis set for excited state orbitals. The energies calculated for the higher excited states will be much poorer in accuracy and probably bear little resemblance to reality. However, our present objective lies in the comparisons between the lowest excitation energies of geometric isomers rather than in accurate predictions of all the excitation energies for individual isomers. Therefore, the approximation used may be considered to suffice for the present purposes, if the differences in the lowest excitation energies calculated for isomers of "normal" butadiene derivatives compare reasonably well with those observed.

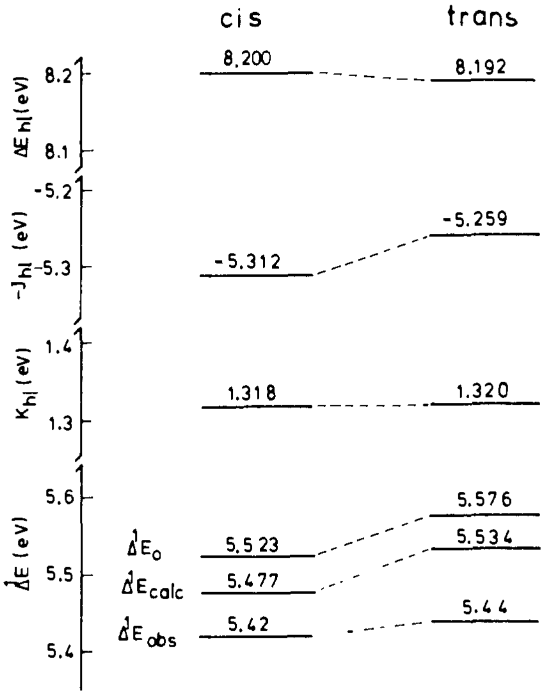


Figure 4. Diagrammatical representation of the contributions of $\Delta\epsilon_{hl}$, J_{hl}, and K_{hl} to the lowest singlet $\pi \rightarrow \pi^*$ excitation energies, Δ^1E, of *cis*- and *trans*-1-cyanobutadienes. Δ^1E_0 indicates the energy calculated without configuration interaction.

We now consider the greater excitation energies for trans isomers as compared with cis isomers. To a first approximation, it will be sufficient to compare the energies of the lowest excited spin configurations $^1\Phi_{h,l}$.[38]

Table V. Lowest Singlet $\pi \rightarrow \pi^*$ Transitions of *trans*-1,3,5-Hexatriene

	Obsd[a]			Calcd[a]		Calcd			
Conformation	Δ^1E, eV	λ_{max}, nm	$10^{-4}\epsilon$, M^{-1} cm^{-1}	Δ^1E, eV	f	Δ^1E_0, eV	J_{hl}, eV	f_x	f_y
s-cis,s-cis	4.35	285	1.35	4.70	0.714	5.224	5.234	0.172	0.682
s-cis,s-trans	4.57	271	1.57	4.88	0.844	5.292	5.183	0.662	0.327
s-trans,s-trans	5.15	241	4.80	5.08	1.461	5.409	5.107	1.450	0.106

[a] Reference 27.

The energy, Δ^1E_0, of the lowest excited singlet configuration above the ground state is formally expressed as

$$\Delta^1E_0 = \Delta\epsilon_{hl} - J_{hl} + 2K_{hl} \tag{4}$$

where $\Delta\epsilon_{hl}$ stands for the energy gap between the lowest vacant and the highest occupied molecular orbitals and where J_{hl} and K_{hl} are the orbital Coulomb repulsion and exchange integrals, respectively. In eq 5 and 6, C_{hr},

$$J_{hl} = \sum_r\sum_s C_{hr}^2C_{ls}^2(rr|ss) \tag{5}$$

$$K_{hl} = \sum_r\sum_s C_{hr}C_{lr}C_{hs}C_{ls}(rr|ss) \tag{6}$$

etc., are the relevant LCAO coefficients, and summations extend over all the atomic orbitals involved.

In Figure 4, the contributions of the three terms $\Delta\epsilon_{hl}$, J_{hl}, and K_{hl} to Δ^1E_0 are diagrammatically compared between the *cis*- and *trans*-1-cyanobutadienes. The orbital energy gap $\Delta\epsilon_{hl}$ is slightly greater for the cis isomer, and the exchange terms K_{hl} are nearly equal for the two isomers. In contrast, the Coulomb repulsion term J_{hl} is noticeably greater for the cis isomer, and its contribution to the relative size of Δ^1E_0 is more than counterbalancing that of $\Delta\epsilon_{hl}$. The net result is that the excitation energy calculated for the cis isomer is smaller.

Exactly the same situation has been confirmed with all the remaining butadiene derivatives. For the sake of easier recognition, the calculated values of J_{hl} are included in Table II. All these results show that the lowest singlet $\pi \rightarrow \pi^*$ excitation energies for trans isomers of terminal-substituted planar butadienes are calculated to be greater than those of the corresponding cis isomers, primarily as a consequence of the greater interorbital Coulomb repulsion J_{hl} in the latter isomers. This may be interpreted if it is assumed that cis isomers experience greater relief from intramolecular electronic repulsion upon excitation. That the J_{hl} values for cis isomers are greater than those for the trans counterparts are obvious from eq 5; the molecular orbitals do not greatly differ between cis and trans isomers, whereas some of the two-center electronic repulsions associated with substituent(s) are greater for cis isomers because of smaller internuclear distances.

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

$$\begin{aligned} f &= 1.085 \times 10^{-5}\nu(r_x^2 + r_y^2) \\ &= f_x + f_y \end{aligned} \tag{7}$$

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. The values of f_x and f_y calculated for isomers of the various butadiene derivatives are given in Table II, where it may be seen that the f_x values differ little between isomers whereas the f_y values are considerably greater for the trans isomers. As a result, the sum $f_x + f_y$ for a trans isomer is greater than that for the corresponding cis isomer, which is compatible with the observation that trans isomers generally have greater extinction coefficients than their cis isomers.

When the lowest excited spin configuration alone is considered, the transition moment length may be written to the zero-differential-overlap approximation as

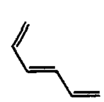
$$r_s = \sqrt{2}\sum_t C_{ht}C_{lt}r_s^t \tag{8}$$

where r_s^t denotes the Cartesian coordinates for the atom t. Obviously, the x-coordinate sets r_x^t are identical for geometric isomers, and hence their calculated f_x values should be nearly equal. The f_y values, on the other hand, tend to be greater for trans isomers. Analysis of the wave functions for 1-substituted butadienes showed that, in general, the product values of $C_{ht}C_{lt}$ for the terminal carbon atom 4 are opposite in sign to those for the atoms located at the end of the substituents (see Table IV). Clearly, these opposing contributions of the terminal atoms render the r_y greater for the trans isomers, in which the differences in r_y^t between the chromophore-end atoms are greater. A similar analysis applies to disubstituted butadienes.

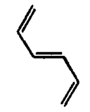
D. Conformational Isomerism. The effect of molecular conformation on the excitation energies of conjugated compounds appears to be related with the effect of geometric structure discussed above. Thus, as has long been recognized, the $\pi \rightarrow \pi^*$ excitation energies calculated for the s-trans conformation of conjugated compounds are greater than those for the corresponding s-cis conformers.[27,34–36]

Allinger and Miller[27] have examined in detail the lowest $\pi \rightarrow \pi^*$ excitation energies of the hexatriene moieties present in various polycyclic molecules. They showed that the stripped chromophore values of λ_{max} for *trans*-hexatriene, which increase in the order of s-trans,s-trans < s-cis,s-trans < s-cis,s-cis, can be reproduced satisfactorily from the CI computations based on the original method of Pariser and Parr.[12]

s-trans, s-trans



s-cis, s-trans



s-cis, s-cis

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(33) The energy lowerings caused by configuration interactions are no more than 1% the energies of $^1\Phi_{h,l}$, and are nearly the same in magnitude for different isomers.

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

(35) M. Klessinger and W. Lüttke, *Z. Electrochem.*, **65**, 707 (1961).

(36) A. Julg and J. C. Donadini, *C.R. Acad. Sci.*, **252**, 1798 (1961).

Table VI. Excited Triplet States of *cis*- and *trans*-1,3-Pentadienes

Geometry	State (i)	Δ^3E, eV Obsd[a]	Calcd	${}^3\Psi_i$[b] $B_{h,l}$	$B_{h-1,l}$	$B_{h,l+1}$
Cis	1	2.78	3.058	0.999	−0.009	0.029
	2		5.843	−0.014	0.722	0.689
	3		6.128	0.026	0.689	−0.722
Trans	1	2.82	3.087	0.999	−0.009	0.027
	2		5.902	−0.012	0.720	0.691
	3		6.196	0.242	0.691	−0.721

[a] Reference 39. The observed values determined in chloroform have been corrected to the vapor phase by adding 0.25 eV. [b] The state functions are expressed as ${}^3\Psi_i = \Sigma_{j \neq k} B_{j,k} {}^3\Phi_{j,k}$.

In the interest in analogy with the effect of geometric isomerism, we have calculated the lowest excited configurational energies, Δ^1E_0, and oscillator strengths, f_x and f_y, for the three planar *trans*-hexatriene conformers. The results are given in Table V, together with the observed data as well as the values calculated by Allinger and Miller.[27] Agreement of our single-configuration values with observation is not as good as that of the CI values obtained by those authors. Nevertheless, we may point out that the excitation energy decreases with the increasing J_{hl} value, just as has been noticed in the comparisons between geometric isomers of conjugated dienes (Table II). A similar correlation appears to hold with the n → π* as well as π → π* transition energies for planar conformers of conjugated carbonyl compounds.[33,37,38]

E. Triplet Excited States. In view of the success in interpreting the effects of geometric structure on the singlet excitation energy of dienes, a brief discussion of the structural effects on the triplet excitation energy seems to be in order.

According to the results of calculations, the lowest triplet excitation energy, Δ^3E, of a diene can also be very well approximated by the lowest configurational energy.

$$\Delta^3E_0 = \Delta\epsilon_{hl} - J_{hl} \qquad (9)$$

Comparison of eq 9 with eq 8 readily leads to the expectation that, so far as the virtual orbital approximation is valid, the difference in Δ^3E between geometric isomers of a "normal" diene will be nearly equal to that in Δ^1E between them, since K_{hl} differ very little between the isomers.

Experimental data which may be put to a test for the above expectation are very meager. To our knowledge, the only pertinent data are those of Kellogg and Simpson,[39] who reported that *cis*- and *trans*-1,3-pentadienes show the singlet–triplet absorption bands at 490 and 483 nm, respectively, in chloroform. The triplet excitation energy of the trans isomer is greater than that of the cis by *ca.* 0.04 eV.

Table VI summarizes the results of calculations for lower excited triplet states of *cis*- and *trans*-1,3-pentadienes. The lowest excitation energy is greater for the trans isomer, as has been expected. In either isomer, the excitation energy calculated is too great as compared with the observed, but this much of disagreement is wholly tolerable in view of the approximate procedure employed. More important here is the difference between the values calculated for the two isomers, *i.e.*, 0.029 eV, which is in close agreement with the observed difference of 0.04 eV.

Concluding Remarks

So far as the 1-substituted and 1,4-disubstituted butadienes which are predominantly in the planar s-trans conformation are concerned, both the energy, Δ^1E, and oscillator strength, f, of the lowest singlet excitation are generally greater for trans isomers than for the corresponding cis isomers, irrespective of the electronic properties, electron donating or attracting, of the substituents involved. The generalization can be rationalized from the semiempirical SCF–MO treatments of the Pariser–Parr–Pople type, in which the effect of geometric structure is reflected only in the placement of the substituents. Within the limits of virtual orbital concept, the smaller excitation energy of cis isomers is understood to be related with the greater orbital Coulomb repulsion integrals J_{hl} between the highest occupied and lowest vacant levels, the differences in the orbital energy gap $\Delta\epsilon_{hl}$ and the orbital exchange integral K_{xl} between isomers being relatively immaterial. It appears that discussion can also be extended to the lowest triplet excitation energy Δ^3E.

Numerical agreements between the theoretical and experimental excitation energies are not necessarily excellent for all the butadiene derivatives investigated. Obviously, the agreements may be improved with deliberate adjustments of the atomic integrals. Further, inclusions of various other factors, such as the core integrals for non-nearest neighbors and the doubly excited spin configurations, might be desirable for the same purposes. Yet, it is our feeling that these elaborations would be no more than superfluous exercise for the present, so far as our main interest is directed toward comparisons between geometric isomers. It may be noted in this connection that the all-valence-electrons treatments in a modified INDO approximation have proved to give results[28] in harmony with those obtained by the present π-electron treatments. Reliability of theoretical justification for the observed spectral features does not appear to be altered by the level of sophistication of the computational procedure used. Hence, any attempt to refine the treatments would, as we feel, be pointless, until the need for rigorous analysis of the structural effects materializes.

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(37) H. Kato, H. Konishi, H. Yamabe, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, **40**, 2761 (1967).

(38) K. Yamaguchi and T. Fueno, *ibid.*, **44**, 43 (1971).

(39) R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965).