methanol which was saturated with hydrogen chloride gas. Methanol was then evaporated under vacuum, leaving a gummy solid. Where possible, the gummy solid was recrystallized from methanol or methanol–petroleum ether (bp 30–60°) to yield white, crystalline solids. The yields, melting points, analytical, and nuclear magnetic resonance (CCl_4) data are given in Table III. In the case of the ethylbenzene and *t*-butylbenzene adducts, the esters were dissolved in benzene and chromatographed on alumina. The benzene eluants yielded solid material pure enough to be recrystallized from methanol–petroleum ether.

Tetracarboxylic Acids.—Tetracarboxylic acids were prepared by refluxing 10–12 g of the alkylbenzene–maleic anhydride adducts in 125 ml of 1.5 *M* potassium hydroxide solution for 4 hr. The cooled solutions were filtered and acidified with hydrochloric acid, yielding solids. The solids were separated, recrystallized from water, and dried. The yields and equivalent weights are given in Table IV.

TABLE IV
TETRACARBOXYLIC ACIDS OF THE ALKYLBENZENE–MALEIC ANHYDRIDE ADDUCTS

Alkylbenzene	Yield, %	Mp, °C	Equiv wt	
			Calcd	Found
Benzene	90	120–350[a]	77.6	78.6
Toluene	58	197–200	81.1	83.0
Cumene	41	182–184	88.1	88.3
C_{10}–C_{13} alkylbenzene	60	258–260	117[b]	115.1

[a] The acid melts, loses water, and forms the anhydride. [b] Based on molecular weight 237 for the alkylbenzene.

Acknowledgment.—The author wishes to thank Dr. L. P. Lindeman for his help in recording and analyzing the nuclear magnetic resonance spectra.

Three-Membered Rings. II. Conjugative Properties and Electronic Spectra of Substituted Stilbene Oxides[1]

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The ultraviolet spectra of a series of *para*-substituted stilbene oxides demonstrate that oxirane transmits electronic effects *via* second-order conjugation from one phenyl group to the other. The spectra of the corresponding bibenzyls and particularly the *para*-substituted styrene oxides serve as references. This transmissive effect of the oxirane ring is found to be consistent with the hyperconjugation description of the *extension* of conjugation in the styrene oxide series. The spectra of some substituted *cis*-stilbene oxides show the expected steric inhibition of conjugative transmission. The thiirane ring in *cis*- and *trans*-stilbene sulfide behaves like the electron-accepting oxirane.

It has recently been shown[2] that oxiranyl and thiiranyl groups act as electron acceptors relative to the benzene ring. This was demonstrated by the ultraviolet spectra of *p*-methoxy and *p*-nitrostyrene oxides and sulfides. The observed red shifts and enhancements of the "first primary" benzene transition[3] were of a magnitude compatible with significant participation in electron delocalization which has been referred to as "extension of conjugation."

The perturbation theory of Petruska[4] and Stevenson[5] lends further support to the qualitative use of electron donor–acceptor resonance structures[6,2] to rationalize the observed conjugative extension of benzene by the three-membered rings when donor or acceptor substituents are present in the *para* position.

We here seek to determine whether "transmission of conjugation" in correspondingly substituted stilbene oxides can be equally satisfactorily demonstrated.

The spectra of *para*-substituted stilbene oxides do show unequivocal conjugative effects beyond the chromophoric expectations from the simply additive constituent-substituted styrene oxides. It is thus possible to ascribe the observed spectroscopic perturbations to "second-order conjugative transmission."

It was found convenient to prepare several of the stilbene oxides from the stilbenes *via* the bromohydrins or in one case from the dibromide. Only 4-methoxy-4′-nitrobibenzyl has not been previously described. This was prepared by reduction of the corresponding stilbene to 4-amino-4′-methoxybibenzyl followed by reoxidation of the amino group with either peracetic or trifluoroperacetic acid.[7]

Experimental Section[8]

Materials.—All of the compounds studied were recrystallized to constant physical properties (melting point, ultraviolet, and infrared spectra), all of which agree with the literature values. The following compounds were obtained commercially or prepared according to published methods: *cis*- and *trans*-stilbene oxide,[9] bibenzyl, 4-nitrobibenzyl,[10] *cis*- and *trans*-4,4′-dinitrostilbene oxide,[11] 4,4′-dinitrobibenzyl,[12] 4-methoxybibenzyl,[13] and 4,4′-dimethoxybibenzyl.[14]

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(1) Preliminary reports of part of this work have been given at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1963, and at the 9th Spectroscopicum Internationale, June 1961, Lyons, France. This work was supported in part by Cancer Research Funds, University of California, and by an Institutional Cancer Research Grant, IN-33D, Allocation 8, from the American Cancer Society. Abstracted, in part, from the Ph.D. thesis of D. Jambotkar.

(2) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *J. Am. Chem. Soc.*, **86**, 4628 (1964).

(3) The "first primary" benzene band (${}^1A_{1g}$–${}^1B_{1u}$) which appears at about 210 mμ is labeled ${}^1A$–${}^1L_a$ in Platt's nomenclature: J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

(4) J. Petruska, *ibid.*, **34**, 1111, 1120 (1961).

(5) P. E. Stevenson, "Systematics of the Electronic Spectra of Conjugated Molecules," John R. Platt and co-workers, John Wiley and Sons, Inc., New York, N. Y., 1964, Paper 32.

(6) S. Nagakura, *J. Chem. Phys.*, **23**, 1441 (1955).

(7) (a) W. Emmons, *J. Am. Chem. Soc.*, **76**, 3470 (1954); (b) *ibid.*, **79**, 5528 (1957). It is interesting that, although a methoxy substituent in the same ring as the amino function is known to cause the reaction to fail, the 4′-methoxy substituent did not produce an untoward effect on the oxidation.

(8) Melting points are corrected. Microanalyses were performed by the Microchemical Laboratory, University of California, Berkeley, Calif.

(9) A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958).

(10) D. N. Kursanov and A. S. Kichkina, *J. Gen. Chem. USSR*, **5**, 1342 (1935).

(11) E. Bergmann and J. Hervey, *Ber.*, **62**, 893 (1929).

(12) S. F. Torf and N. V. Khromov-Borisov, *Zh. Obshch. Khim.*, **24**, 1674 (1954).

(13) R. Perrot and P. Wodey, *Compt. Rend.*, **240**, 100 (1955).

(14) N. J. Leonard and S. Gelfand, *J. Am. Chem. Soc.*, **77**, 3269 (1955).

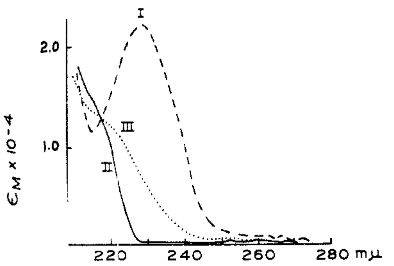


Figure 1.—Ultraviolet spectra of *trans*-stilbene oxide (I), bibenzyl (II), and *cis*-stilbene oxide (III) in ethanol.

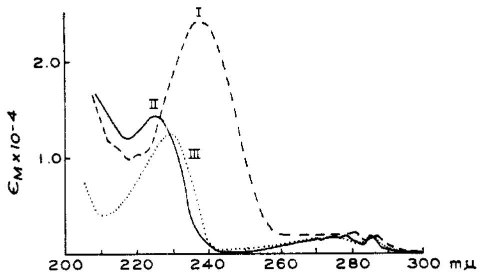


Figure 2.—Ultraviolet spectra of 4-methoxy-*trans*-stilbene oxide (I), 4-methoxybibenzyl (II), and 4-methoxystyrene oxide (III) in hexane.

4-Amino-4′-methoxybibenzyl.—*trans*-4-Methoxy-4′-nitrostilbene (12.3 g, 0.05 mole) in ethanol was reduced over Raney nickel at 40 psi for 5 hr at room temperature to give, after crystallization from hexane, 0.3 g (82%) of 4-amino-4′-methoxybibenzyl, mp 96–97°. *Anal.* Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.04; H, 7.51; N, 6.45.

4-Methoxy-4′-nitrobibenzyl.—Hydrogen peroxide (0.2 mole, 90%) was added to trifluoroacetic anhydride (0.24 mole) in 150 ml of dichloromethane at 0°.[7a] After stirring for 5 min and warming to room temperature, there was added dropwise 11.4 g (0.05 mole) of 4-amino-4′-methoxybibenzyl in 50 ml of dichloromethane. After addition was complete the reaction mixture was heated under reflux for 1 hr. The organic phase was washed with water and 10% sodium bicarbonate, dried over sodium sulfate, and concentrated under vacuum. The residue was crystallized from 50% methanol to give 8.9 g (69%) of 4-methoxy-4′-nitrobibenzyl, mp 77.5–78°. *Anal.* Calcd for $C_{15}H_{15}NO_3$: C, 70.0; H, 5.8; N, 5.4. Found: C, 70.2; H, 5.7; N, 5.6.

When the amine (11.4 g, 0.05 mole) in chloroform was oxidized with peracetic acid[7b] prepared from 90% hydrogen peroxide (0.25 mole), acetic anhydride (0.3 mole), and 1 drop of sulfuric acid, the yield was 9.8 g (76%).

***trans*-4-Methoxy-4′-nitrostilbene Oxide.**—4-Methoxy-4′-nitrostilbene (12.7 g, 0.05 mole) in 60% aqueous dioxane was treated with N-bromoacetamide (8.3 g, 0.06 mole) in 40 ml of 50% *t*-butyl alcohol. The crude bromohydrin (16.2 g, mp 107–110°) obtained by addition of ice, was treated with methanolic potassium hydroxide to give, after crystallization from ethanol, 7.45 g (61%) of the oxide, mp 138–139°, identical with a sample prepared from *p*-nitrobenzyl chloride and anisaldehyde according to the method of Bergmann and Hervey.[11]

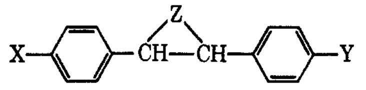
***trans*-4-Nitrostilbene Oxide.**—By a similar procedure, 10.5 g (0.05 mole) of *trans*-4-nitrostilbene was converted to the oxide, mp 127–127.5° (lit.[11] mp 125–126°) in 70% yield *via* the bromohydrin (crude yield 17.0 g, mp 145–150°).

***cis*-4-Nitrostilbene Oxide.**—In 25 ml of 60% methanol *cis*-4-nitrostilbene (1.0 g, 5 mmoles) underwent reaction with 0.85 g (6 mmoles) of N-bromoacetamide to give an oil which solidified (mp 90–130°) when treated with 10 ml of 10% potassium hydroxide. Fractional crystallization from aqueous methanol gave 0.25 g (22%) of *trans*-4-nitrostilbene oxide, mp 126–128°, 0.45 g (38%) of *cis*-4-nitrostilbene oxide, mp 68.5–69°, identical with the product obtained by the method of Chrzescinski,[15] mp 69–70° (lit.[15] mp 74–76°).

***trans*-4-Methoxystilbene Oxide.**—To 10.5 g (0.05 mole) of *trans*-4-methoxystilbene in 125 ml of aqueous dioxane was added 8.3 g (0.05 mole) of N-bromoacetamide in 40 ml of 50% dioxane. This suspension was warmed on a steam bath until a clear solution was obtained (1–2 min), cooled immediately, and treated with 7.5 g of potassium hydroxide in water. The precipitate was collected and crystallized from hexane to give 5.1 g (45%) of oxide, mp 82–83°, identical with a sample prepared by treatment of 4-methoxystilbene dibromide with base according to the method of Curtin.[16]

TABLE I

ULTRAVIOLET SPECTRAL DATA[a] FOR



X	Y	Z[b,c]	λ_1, mμ	$\epsilon_1 \times 10^{-3}$	λ_2, mμ	$\epsilon_2 \times 10^{-3}$
H	H	O-*t*[d]	228	23.5	267	0.90
H	H	O-*c*[d]	218[e]	12.3	261	0.47
H	H	2H[d]	215[e]	12.2	259	0.45
OCH_3	H	O-*t*	238	24.2	287	1.79
					280	2.08
OCH_3	H	2H	225	14.4	285	1.90
					278	2.00
NO_2	H	O-*t*	216	18.0	274	15.3
NO_2	H	O-*c*	. . .	. . .	268	10.6
NO_2	H	2H	217[e]	12.0	268	12.5
NO_2	OCH_3	O-*t*	230	17.6	286	14.6
NO_2	OCH_3	2H	218	15.1	269	12.7
			214	15.0		
OCH_3	OCH_3	O-*t*	242	31.3	279	5.40
OCH_3	OCH_3	2H	225	17.0	279	3.90
NO_2	NO_2	O-*t*[f]	216[e]	15.0	286	24.9
NO_2	NO_2	O-*c*[f]	215[e]	14.4	273	19.2
NO_2	NO_2	2H[f]	214[e]	15.0	276	20.4
H	H	S-*t*[g]	238	17.0	270	1.40
H	H	S-*c*[g]	226	10.6	268	0.80
4-NO_2-styrene oxide			216	9.15	265	11.9
4-CH_3O-styrene oxide			230	12.4	279	1.67

[a] In hexane unless otherwise noted. [b] *t* = *trans* and *c* = *cis*. [c] O = oxygen, S = sulfur. [d] In ethanol, little different from hexane. [e] Shoulder. [f] In ethanol, insufficiently soluble in hexane. [g] In ethanol: R. Ketcham and V. P. Shah, *J. Org. Chem.*, **28**, 229 (1963).

***trans*-4,4′-Dimethoxystilbene Oxide.**—Treatment of *trans*-4,4′-dimethoxystilbene (2.4 g, 0.01 mole) in chloroform with bromine (2.4 g, 0.015 mole) in 10 ml of chloroform gave 3.5 g of crude dibromide, mp 180–181°. This was dissolved in 15 ml of dioxane–water (2:1) and treated with 2 g of sodium hydroxide in 5 ml of water on a steam bath for 10 min. The reaction mixture was poured over ice and the precipitate was collected and crystallized twice from hexane to give 1.0 g (40%) of *trans*-4,4′-dimethoxystilbene oxide, mp 140–141°, (lit.[17] mp 141–142°).

Ultraviolet Spectra.—The spectroscopic data in Table I were obtained from measurements in hexane as previously described.[2] The spectra were also measured in 95% alcohol in order to characterize and differentiate some superimposed bands. (The methoxy-substituted oxides were unstable in the more polar solvents. The kinetics of hydrolysis of *trans*-4-methoxystilbene oxide were studied and found to be first order. Stability was enhanced in weakly alkaline solution.)

Discussion

Comparison of the spectra of the stilbene oxides with those of the corresponding bibenzyls in Figures 1 and 2 and in Table I clearly shows the bathochromic shift and enhanced absorption characteristic of "conjugative" substituents on the $^1A_{1g}$–$^1B_{1u}$ benzene band.[18] For

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[15] O. Chrzescinski, Dissertation, Strassburg, 1911, p 37.

[16] D. Y. Curtin, A. Bradley, and Y. G. Hendrickson, *J. Am. Chem. Soc.*, **78**, 4064 (1956).

[17] G. Henne and A. Bruylants, *Bull. Soc. Chim. Belges*, **57**, 320 (1948).

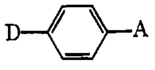
[18] (a) L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957); (b) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 416.

example in *trans*-stilbene oxide or in *trans*-methoxystilbene oxide the maxima shift toward the red, $\Delta\lambda = 13$ mμ, relative to the corresponding bibenzyls and the molar extinction increases by a factor of approximately 2 in each case.

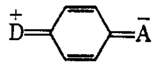
To estimate more surely the degree of chromophoric contribution ascribable to transmission *via* second-order conjugative perturbation[5] it is more significant to compare the red shift and intensities of the stilbene oxides with the corresponding styrene oxides. The "first primary" absorption band of styrene oxide lies below 220 mμ [between 212 and 217 mμ, (ϵ 7000)].[2,19] Consequently, the spectrum of *trans*-stilbene oxide curve I in Figure 1 is seen to be dramatically enhanced comparatively; it is shifted more than 10 mμ and has about a threefold increase in molar extinction.

In Figure 2 the spectrum of *trans*-4-methoxystilbene oxide (λ_{max} 238 mμ) likewise shows a progressive enhancement over 4-methoxystyrene oxide (λ_{max} 230 mμ, $\Delta\lambda = 8$ mμ), and a twofold increase in molar extinction. 4-Methoxystyrene oxide has been found to produce a bathochromic shift ($\Delta\lambda = 7$ mμ) relative to 4-methylanisole with an increase of approximately 50% in molar extinction.[2] Thus the "total" shift of the "first primary" band in *trans*-methoxystilbene oxide, due to the presence of the three-membered ring, can be taken as the sum of extensive and transmissive effects, $\Delta\lambda = 15$ mμ, with a threefold increase in molar extinction.

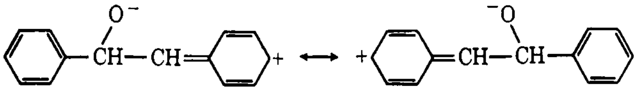
Because in either of the above cases the spectrum of the stilbene oxide is enhanced over the corresponding styrene oxide in a clearly conjugative substituent manner[5,18] it can be concluded that there is "transmission" of second-order conjugation *via* charge-transfer perturbation extending from one phenyl group to the other. As in the case of the styrene oxides, *recognizing that the oxirane ring acts as an electron acceptor*,[2] these spectral effects may be seen to be consistent with the appropriate charge-transfer contributions. Thus, for *trans*-stilbene oxide, structures I and II are equivalent and taken together represent an identical D–A (donor–acceptor) pair as described by Nagakura[6] and Stevenson[5] which lowers the energy of the charge-transfer state and thus produces an enhanced "second-order conjugative perturbation of the ^1L_a state"[5] attributed to the mixing of the wave functions with the low-lying charge-transfer (quinoidal) state.[20] Structure III also may make a contribution to transmission of conjugation but it is difficult to assess relatively.



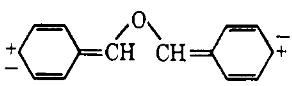
ground state



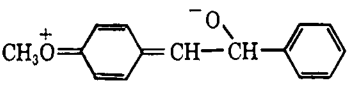
charge-transfer state



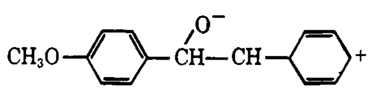
I II



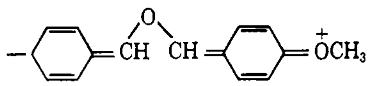
III



IV



V



VI

In the case of the *trans*-methoxystilbene oxide, structures IV and V are unequal in energy and consequently structures IV and VI will contribute relatively more significantly. That structures like VI contribute, is made even more likely in considering the *trans*-4-nitrostilbene oxide because in this case as shown earlier[2] the electronegative oxirane ring does not conjugatively extend the nitrobenzene chromophore. (The spectra of 4-nitrostyrene oxide and 4-alkylnitrobenzenes are nearly identical.) Since styrene oxide contributes weakly relative to nitrobenzene, the fact that 4-nitrostilbene oxide is enhanced over 4-nitrobibenzyl [λ_{max} 268 mμ (ϵ 12.5 × 10^3) to λ_{max} 274 mμ (ϵ 15.3 × 10^3) with increased half-width] means a transmissive effect occurs and in hyperconjugative[21] terms it primarily

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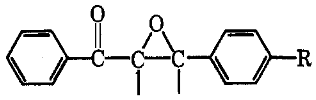
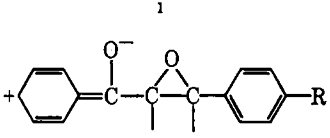
[19] M. T. Rogers, *J. Am. Chem. Soc.*, **69**, 2544 (1947).

[20] In contrast with the second-order conjugative perturbation, the second-order inductive perturbation lowers both the ground state and the excited state; *cf.* ref 5, particularly Figure 5.

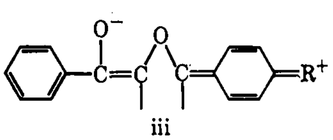
[21] Rogers[19] first presented the hyperconjugative concept to account for the observed chromophoric extension of conjugation in styrene oxide. He proposed hyperconjugative contributions involving either positive or negative charge on the oxygen atom. In this limited study, he did not attempt to assess the relative importance of the two forms. Cromwell, *et al.*,[22] introduced hyperconjugative concepts and offered extensive chromophoric evidence of "transmission of conjugation." Cromwell attributed *only* electron-donor character to the oxirane ring. However, see A. Padwa, L. Hamilton, and L. Norling, *J. Org. Chem.*, **31**, 1244 (1966). The evidence which we present here might be taken to confirm Cromwell's conclusion, but the validity of his conclusion derived from his chromophoric evidence seems uncertain. In each case presented in the series of papers, the competing first-order conjugation would swamp or eliminate chromophoric manifestation of the second-order conjugative effect. For example, in chalcone oxides (i), chromophoric (π–π^*) contributions from first-order conjugation of the aryl ketone (type ii) would either abolish or make of dubious significance perturbation effects from the second-order "transmission" of conjugation to be ascribed to iii, nor would one expect to find definitive "extension of conjugation" effects arising from the electron acceptor nature of the oxirane as in iv. First- and second-order inductive perturbations variably affecting both ground and excited states[5,20] in the various cases presented in the series would either overshadow the magnitude of the second-order conjugative chromophoric shift or would be indistinguishable. The contradictory effect[22a] when R is methoxy emphasizes the inadequacy of this π–π^* transition for demonstrating transmission of conjugation. An example in which a second-order conjugative effect is eliminated by a first-order competing conjugation is the disappearance in the spectrum of phenylacetic acid of the pronounced band at 300 mμ in phenylacetone.[23] Similarly, the absorption at 251 mμ (ϵ 1150)



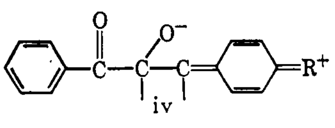
i



ii

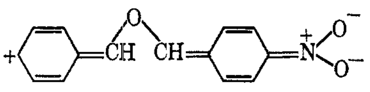


iii



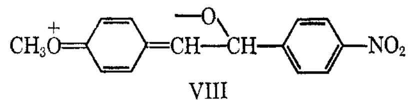
iv

arises from VII and is manifested as an enhancement of the nitrobenzene chromophore.

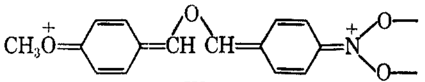


VII

trans-4-Methoxy-4′-nitrostilbene oxide was analyzed more completely to measure the hyperconjugative transmission. In Figure 3, curve III, the additive spectra of 4-nitrostyrene oxide and 4-methoxystyrene oxide may be compared with curve I, the spectrum of *trans*-4-methoxy-4′-nitrostilbene oxide. In curve III the bands at 214 and at 266 mμ may be identified with the nitrobenzene chromophore in 4-nitrostyrene oxide,[25] whereas the inflections between 270 and 286 mμ superimposed on the 4-nitrostyrene oxide band, are readily identified with the enhanced anisole chromophore in 4-methoxystyrene oxide.[2] If there were no transmissive effect through the oxirane ring, curves III and I would be expected to be nearly identical. The broad transition in curve I may be readily correlated with a significantly enhanced nitrobenzene chromophore. By taking advantage of the differential solvent effect shown in Figure 4[2,27] it becomes evident that the marked enhancement of the spectrum of the oxide over the bibenzyl arises from the perturbation of the nitrobenzene chromophore in curve III, Figure 3, whereas the anisole-like 4-methoxystyrene oxide chromophore is unenhanced or slightly weaker as seen from study of the shorter wavelength region. This is understandable as a secondary conjugative transmission by the oxirane ring and can be rationalized qualitatively in terms of contributions from VIII and IX.



VIII



IX

The evidence of transmission of conjugation by the oxirane ring derived from its perturbation of the well-understood benzene spectrum indicates that the apparent anomalies[22a,23b] reported earlier arise from the unsuitable and overly complex chromophores which were used. Also, it must be recognized as a second-order effect and cannot be unambiguously observed except in conjunction with properly constituted primary conjugative systems.

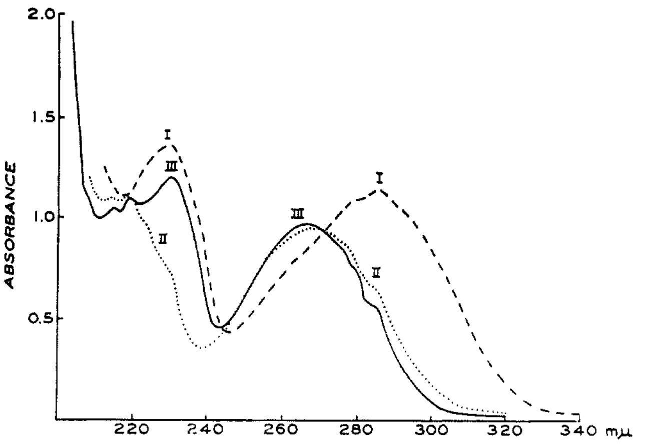


Figure 3.—Ultraviolet spectra of 4-methoxy-4′-nitro-*trans*-stilbene oxide (I), 4-methoxy-4′-nitrobibenzyl (II), and equimolal mixture of 4-methoxystyrene oxide and 4-nitrostyrene oxide (III); $7.8 \times 10^{-5} M$ in hexane.

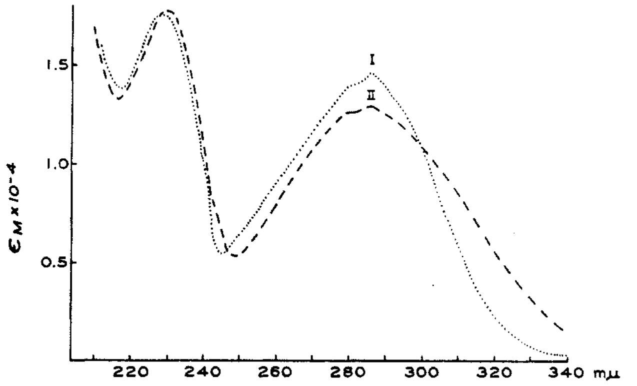


Figure 4.—Ultraviolet spectra of 4-methoxy-4′-nitro-*trans*-stilbene oxide in hexane (I) and in ethanol (II).

The differences in the spectra of various pairs of *cis*- and *trans*-stilbene oxides also constitute an important measure of the conjugative properties of the oxirane ring. In every case the absorption bands of the *trans* isomers are markedly enhanced over those of the *cis* isomers. Such differences are best attributed to the conjugative properties of the oxirane ring and can be interpreted, in agreement with Walsh,[28] Cromwell,[22] and others,[29] as indicating a steric requirement for delocalization. The same spectral relationships were observed for *cis*- and *trans*-stilbene sulfide.[30] These conclusions are in contrast with that of Goodman and Eastman[31] on the apparent absence of a steric requirement for conjugation in certain phenylcyclopropanes.[32]

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in ethyl 1-acetyl-2-vinylcyclopropanecarboxylate disappears when the acetyl group is replaced by a carbethoxy group.[24]

(22) (a) N. H. Cromwell, F. H. Schumacher, and J. L. Adelfang, *J. Am. Chem. Soc.*, **83**, 974 (1961); (b) for a review, see N. H. Cromwell, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **19**, 215 (1958); (c) A. Rosowsky, "Chemistry of Heterocyclic Compounds," Vol. 19, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 1-147.

(23) (a) W. D. Kumler, L. A. Strait, and E. L. Alpen, *J. Am. Chem. Soc.*, **72**, 1463, 4558 (1950); (b) for other examples, see Mariella and Raube, *ibid.*, **74**, 521 (1952); G. W. Perold, *J. S. African Chem. Inst.*, **6**, 22 (1953).

(24) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 1799, 1803 (1953).

(25) The intense transition with λ_{max} at 266 mμ has been considered the displaced enhanced benzene transition ${}^1A_{1g}-{}^1B_{1u}$ (${}^1A-{}^1L_a$) owing to the conjugative ${}^1B_{1u}$ nitro substituent.[26]

(26) Reference 18b, p 255.

(27) (a) W. M. Schubert, H. Steadly, and J. M. Craven, *J. Am. Chem. Soc.*, **82**, 1353 (1960); (b) W. M. Schubert and J. M. Craven, *ibid.*, **82**, 1357 (1960).

(28) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(29) J. F. Music and F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5256 (1950).

(30) See R. Ketcham and V. P. Shah in Table I, footnote *g*.

(31) A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

(32) The substituted indane systems used may be self-defeating in that simple theory to date[33] is inadequate and the strain in the adjacent ring might modify the hybridization in the cyclopropyl *exo* bonds with a consequent decrease of the π enrichment in the cyclopropane ring bonds.

(33) (a) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 3161 (1963); (b) W. J. Flygare, *Science*, **140**, 1181 (1963).