

Conformational Analysis. CIV. Structures, Energies, and Electronic Absorption Spectra of the $[n]$ Paracyclophanes^{1,2}

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Abstract: The $[n]$ paracyclophanes (with n equals 5–10) have been studied by a previously described force-field method. The possible conformations are discussed, and structures and strain energies are predicted. For the two examples where the crystal structure is known, the calculations are in good agreement with experiment. By carrying out a doubly excited configuration interaction calculation on the π system, the electronic spectra are calculated. The agreement with the known members of the series is fairly good.

The $[n]$ paracyclophanes are a group of compounds which have as their distinguishing feature a benzene ring, the para positions of which are joined together by means of a cyclic side chain. This series of compounds has been of particular interest, because as n gets sufficiently small, the benzene ring is bent from planarity.³



The known paracyclophanes, with values of n from 16 down to 10, have not occasioned much surprise. They have been prepared by methods which are reasonably straightforward, and they do not seem to exhibit very unusual physical properties. As the value of n decreases below 9, the synthesis of the molecules becomes more esoteric, but the [8]-,⁴ [7]-,^{3,5} and [6]paracyclophanes⁶ have now been synthesized.

The physical property which was early observed to be a function of ring bending is the ultraviolet spectrum. Increasingly out-of-plane deformation of the benzene ring leads to an increasing red shift of the three transitions observed in the ultraviolet region, and these have been studied from a theoretical⁷ point of view.

Another physical property of interest is the nmr spectrum. It might be supposed that the side chain protons which are pushed down into the π cloud of the aromatic ring will be greatly shielded, and this has been found. It might also be supposed that as the ring is bent into a tub, the ring current will be inhibited, and the aromatic protons will also be more shielded. The effect is apparently too small to observe with the compounds so far studied.

Finally, the details of the structures of these ring systems are of interest. In general, shortening the chain causes the benzene ring to bend more and more into the shape of a boat. X-Ray structures are available for

the carboxy derivatives of the [7]-¹ and [8]paracyclophanes.⁸ The side-chain conformations for the various paracyclophanes present some interesting problems. These have been studied in some detail in the present work.

In an earlier paper⁹ a force-field calculational method was described which was applied to many compounds containing both aromatic and aliphatic parts. The same basic force field was used in the present calculations. One change has, however, been made in the method used for the calculation of the force constants for torsion. These were earlier taken to be proportional to the square of the bond order, simply because the limited available data could be fit with such a function. Further considerations now indicate that the torsional constants should be proportional to the bond order to the first power times the resonance integral (β_{ij}) for the planar form. This function should work adequately for something like ethylene or substituted ethylenes where the bond is of a usual length (corrected for by the β term). For a conjugated system, this will not be sufficient, however. This can perhaps best be seen by examining butadiene. As a rotation about the central bond occurs, the bond order will fall off, and if that were all that happened, then our equation would be correct. However, the energy of the system is not raised by that great an amount, because the bond orders of the 1,2 and 3,4 bonds increase with the decreasing bond order of a 2,3 bond. This means that the energy increase upon rotation is less than would be expected from simply an examination of the 2,3 bond, and what one must in fact do is look at the energy increase which results from rotation about the 2,3 bond and subtract from this the energy decrease which is gained by the increase in bond order of the other bonds.

The torsional constant (k_{ij}) can then be written

$$k_{ij} = f \times 60 \times P_{ij}\beta_{ij}(0^\circ) \text{ kcal/mol}$$

where k_{ij} is the torsional constant across bond $i-j$, $P_{ij}\beta_{ij}(0^\circ)$ is $P\beta$ product across bond $i-j$ in the corresponding π -planar conformation, and

$$f = \frac{\sum_{ij} P_{ij}\beta_{ij}(0^\circ) - P_{ij}\beta_{ij}(\text{real})}{\sum_{ij} P_{ij}\beta_{ij}(0^\circ)(1 - \cos^2 \omega_{ij})}$$

where the sum is over all π bonds, $P_{ij}\beta_{ij}(\text{real})$ is the $P\beta$

(1) For paper CIII, see N. L. Allinger, T. J. Walter, and M. G. Newton, *J. Amer. Chem. Soc.*, **96**, 4588 (1974).

(2) Supported by Grant GP-15263 from the National Science Foundation.

(3) For a recent summary of the literature, see ref 1.

(4) D. J. Cram and G. R. Knox, *J. Amer. Chem. Soc.*, **83**, 2204 (1961); N. L. Allinger and L. A. Frieberg, *J. Org. Chem.*, **27**, 1490 (1962).

(5) N. L. Allinger and T. J. Walter, *J. Amer. Chem. Soc.*, **94**, 9267 (1972); A. D. Wolf, V. V. Kane, R. H. Levin, and M. Jones, Jr., *ibid.*, **95**, 1680 (1973).

(6) M. Jones, Jr., and V. V. Kane, personal communication.

(7) N. L. Allinger, L. A. Frieberg, R. B. Hermann, and M. A. Miller, *J. Amer. Chem. Soc.*, **85**, 1171 (1963).

(8) M. G. Newton, T. J. Walter, and N. L. Allinger, *J. Amer. Chem. Soc.*, **95**, 5652 (1973).

(9) N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **95**, 3893 (1973).

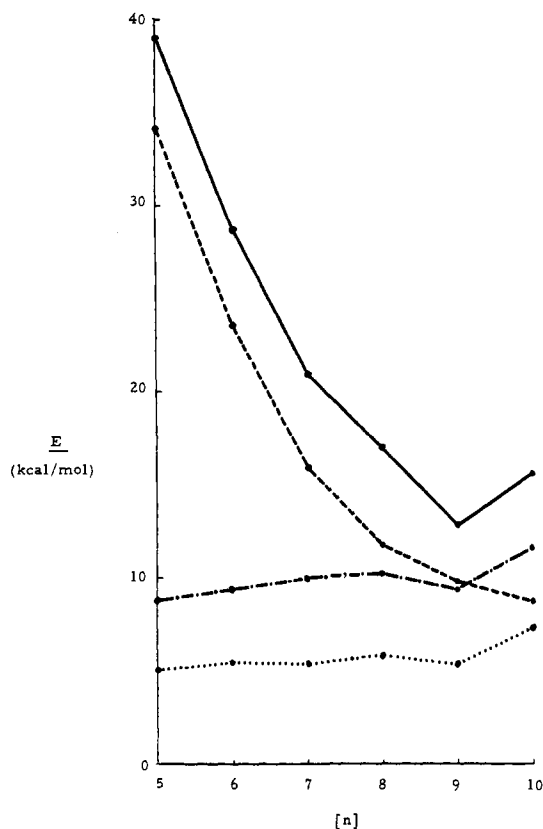


Figure 1. Strain energy and steric energy components in the $[n]$ -paracyclophanes: strain energy, —; torsional energy, ----; bending energy, ·····; VDW energy, -·-·-.

product across bond $i-j$ in the real (distorted) π system, and ω_{ij} is the dihedral angle across bond $i-j$. The numerator is the net change in π energy as the molecule goes from the planar to distorted geometry and the denominator is the second-order torsional functions estimation of this same quantity, according to our molecular mechanical model.

In principle the above treatment of torsion should be better than what was used previously and we have applied it to a number of nonplanar compounds. It was found that for compounds previously reported there were no significant changes. For compounds which have severe torsional strain about double bonds, such as the smaller paracyclophanes, the original formulation led to excessive rigidity. The present method works better for such highly deformed systems.

We applied this molecular mechanical model to the study of the paracyclophanes in which $n = 10, 9, 8, 7, 6,$ and 5 . An examination of models indicates that the odd paracyclophanes may have C_s or C_2 symmetry, with the central methylene group in the bridge of the latter either pointing up (u) or down (d). The even paracyclophanes will preferentially have C_2 symmetry owing to the ethane-type eclipsing which must occur in the mirror conformers.

Calculated structural features for the molecules studied are listed in Table I. The strain energies (as previously defined¹⁰) and the important steric energy components for the preferred conformations are

(10) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971).

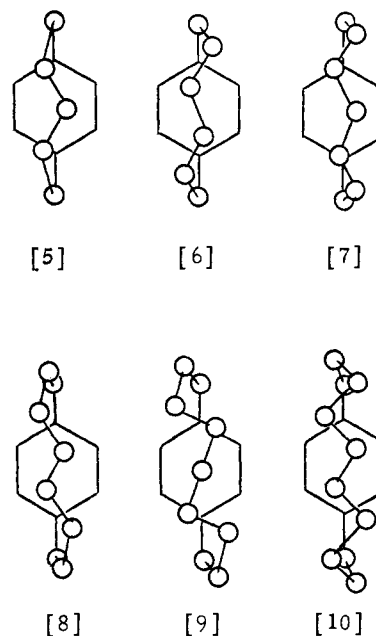


Figure 2. Preferred conformations of the $[n]$ paracyclophanes.

Table I. Relative Strain Energies and Structural Features of the $[n]$ Paracyclophanes

Compound	Strain energy, ^a kcal/mol	Ring angle ϕ , deg	Side-chain angle α , deg	Av aliphatic C-C-C angle, deg
[5], C_s	39.05	26.5	28.6	115.9
[5], C_2 (u)	48.34	29.9	31.8	118.6
[5], C_2 (d)	57.73	26.6	24.6	127.6
[6], C_2	28.74	22.4	18.1	115.1
[7], C_s	20.91	18.2	10.2	115.3
[7], C_2 (u)	23.16	20.8	15.1	114.6
[7], C_2 (d)	29.96	23.8	11.6	118.3
[8], C_2	16.83	12.5	5.1	115.4
[9], C_s	16.51	4.4	2.0	115.8
[9], C_2 (u)	12.70	8.5	4.0	114.6
[9], C_2 (d)	14.22	10.4	4.8	115.4
[10], C_2	15.48	8.4	-4.4	116.5

^a Calculated according to the method outlined in ref 10. *p*-Xylene was used as the strainless reference compound.

graphed as a function of n in Figure 1. The conformations themselves are illustrated in Figure 2.

In the smaller paracyclophanes, the strain energy is dominated by the folding of the aromatic ring (reflected in the torsional energy component). As n increases, this deformation is soon relieved so that in the [9]- and [10]paracyclophanes, the strain becomes quite sensitive to the bending and van der Waals interactions. It might be noted that the odd behavior of these latter two curves is quite analogous to their behavior in the C-4 to C-12 aliphatic ring series.¹⁰ We might expect, in fact, that the strain in the paracyclophanes will increase as n becomes greater than 10, until a maximum is reached, and then eventually decrease as the aliphatic bridge becomes large enough to avoid cross-ring interactions.

Perhaps one might not have expected from looking at models that the strain energies in the [9]- and [10]paracyclophanes would be as high as they are (12.7 and 15.5 kcal/mol, respectively). These large strain energies are mainly due to torsion, because of poor conformations in

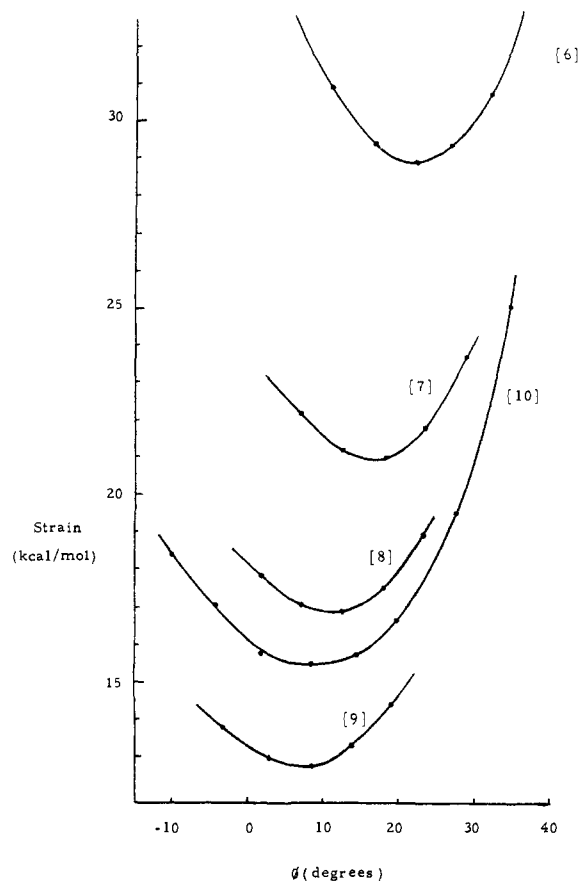


Figure 3. Ring bending potentials for the $[n]$ paracyclophanes.

the side chain. The problem is analogous to that found in the medium-ring alicyclics. There simply is no strainless conformation into which the side chain can be arranged and, hence, these large strain energies. It is perhaps also somewhat unexpected that the [10]paracyclophane is more strained by nearly 3 kcal than [9]paracyclophane. This is, again, because of these torsional arrangements. Ten atoms cannot be fit around in the prescribed cycle as well as nine can, with respect to these torsions. Bond stretching is not an important source of strain in any of these compounds.

In view of the difficulties encountered in synthesizing the smaller cyclophanes,³ we were especially interested in the calculated strains of [6]- and [5]paracyclophanes (28.0 and 39.1 kcal/mol, respectively). For the [6]paracyclophanes, this value is low enough that one might expect the compound to be isolable if the technical details of synthesis can be arranged. Recent work, in fact, indicates this to be the case.⁶ By way of comparison, norbornadiene, calculated to have 31.6 kcal/mol of strain,¹¹ is a reactive but isolable olefin.

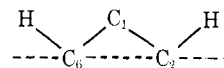
The much higher strain of [5]paracyclophane, however, poses a serious synthetic problem. It's not certain that the compound will be thermodynamically stable. Thus, it might spontaneously close to a prismane, for example. If the molecule is stable enough to be isolable, there is again the problem of a synthetic method which is suitable for its preparation. The method used by Jones^{5,6} would introduce the entire amount of strain in one step. It's not clear that so

(11) N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972).

great an energy barrier can be overcome in a single step. If the compound were prepared by ring contraction from the next higher homolog, it would only be necessary to introduce 11.1 kcal in the crucial ring contraction step. The method previously used⁵ (the Wolff rearrangement) has more than enough energy available to accomplish this ring contraction, but it is possible that a hydride migration may, in fact, become the exclusive reaction of the diazo compound under these circumstances. Thus, it would seem unclear as to whether or not the [5]paracyclophane will be achievable synthetically, nor is it clear which approach is the best to use. These matters seem to require further experimental work.

A point of interest is that in [5]- and [7]paracyclophane the axially symmetric conformer is of higher energy than the one which is symmetric about a mirror plane. In the case of [9]paracyclophane, the opposite is true and the axially symmetric conformer is the more stable.

Several structural features are worth noting, the most unusual being the location of the aromatic protons. Viewing the aromatic ring from the front, these protons are calculated to be above the common plane of the ring rather than below it, as might have been expected.



This displacement ranged from 0.13 Å in [5]paracyclophane to 0.03 Å in the [10] homolog. In agreement with our calculations, the crystal structures of [8]- and [2,2]-paracyclophane show similar type displacements.^{8,12}

The angles ϕ and α , included in Table I, concurrently decrease as n increases, as would be expected. An interesting point is seen in [10]paracyclophane. The pucker of the benzyl carbon (α) is opposite the direction of the pucker of the ring, indicating that the latter is probably caused by VDW interactions between the bridge hydrogens and the ring carbons rather than being forced by the shortness of the bridge, as is the case in the smaller paracyclophanes. The bond lengths and bond angles of the benzene ring do not show any significant variations throughout the group of compounds studied; however, the aliphatic C-C-C angles show a slight decrease as n increases, reaching a minimum for $n = 9$ and then increasing for $n = 10$.

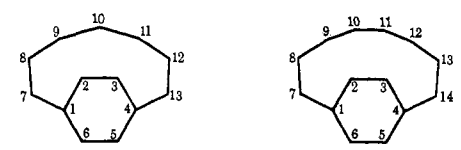
Potential curves for the deformation of the aromatic ring were calculated for the most stable conformer of each cyclophane and are shown in Figure 3. The curves are generally parabolic in shape and are shallow enough to allow a very wide amplitude of ring oscillation ($\Delta\phi$ of 20–40° at room temperature).¹³ The minimum for [10]paracyclophane is noticeably flatter than the others, changing less than 0.2 kcal/mol over a 10° range of ring bending. When X-ray structures become available for the [9]- and [10]paracyclophanes, it would therefore be no surprise if the crystalline geometries differ significantly from our calculated gas-phase structures, since crystal packing forces may be quite large compared to the modest ring bending potentials. For comparison with what data are available, the calculated

(12) H. Hope, J. Bernstein, and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **28**, 1733 (1972).

(13) It seems not to have been widely appreciated before [H. Wynberg, W. C. Nieupoort, and H. T. Jonkman, *Tetrahedron Lett.*, 4623 (1973)] that the ordinary vibrational motions of the benzene ring cause it to deviate from planarity by perhaps 10° or so at room temperature.

and crystal structures of [7]- and [8]paracyclophane are listed in Table II. As can be seen, the agreement is quite good.

Table II. Experimental and Calculated Structures of [7]- and [8]Paracyclophane



	[7]		[8]	
	Exptl ^a	Calcd	Exptl ^b	Calcd
Symmetry	C _s	C _s	C ₂	C ₂
φ, deg	17	18.2	9.1	12.5
α, deg	6.5	10.2	5.6	5.1
Aliphatic C-C-C, deg	111-117	110.2-119.2	110.4-116.3	111.8-117.0
C ₂ ...C ₁₀ , Å	3.15	3.39	3.36	3.37
C ₆ ...C ₁₀ , Å	3.65	3.59	3.61	3.65
ω ₉₋₁₀₋₁₁₋₁₂ , deg		148.2	156.1	163.6

^a Reference 3. ^b Reference 8.

Using the geometries generated by our mechanical model, the electronic spectra for the paracyclophane series were then calculated. The VESCF method used was basically the same as that utilized in the molecular mechanics scheme, the only real difference being changes in the two-center repulsion integrals. As an additional feature, configuration interaction, taking all singly and doubly excited configurations into account, was added. The details of the method (VESCF-CI) and applications of it to calculations of electronic spectra have been presented in earlier papers.¹⁴⁻¹⁸

It had earlier been noticed that the two-center repulsion integral, used in the original VESCF-CI scheme,¹⁴ gave too large a value for given distances and a modified formula was proposed

$$\gamma_{12}(\text{emp}) = \gamma_{12}(\text{theor}) - 0.5S_{12}(A + 1)/(A + S_{12}) \times [\gamma_{11}(\text{theor}) - \gamma_{11}(\text{emp}) + \gamma_{22}(\text{theor}) - \gamma_{22}(\text{emp})]$$

where A was set equal to 2.5.¹⁶ The modified version, applied to benzene, gave calculated transitions in better agreement with experiment than the original one, but there was still a significant error of 0.33 eV in the lowest energy transition. A closer analysis also showed that the modified repulsion integral has too large a slope to make it possible to accurately calculate the electronic spectrum of benzene. We found that using a slightly lower value for the one-center repulsion integral, $\gamma_{11}(\text{emp})$, we could get more suitable values for $\gamma_{12}(\text{emp})$, making it possible to reproduce the benzene spectrum to within 0.14 eV and at the same time reproduce the spectra of linear olefins, such as ethylene, *cis*-2-butene, and butadiene, to within the same limits of error. The value for $\gamma_{11}(\text{emp})$ used in the present calculations is

(14) N. L. Allinger and J. C. Tai, *J. Amer. Chem. Soc.*, **87**, 2081 (1965).

(15) N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theor. Chim. Acta*, **8**, 101 (1967).

(16) J. C. Tai and N. L. Allinger, *Theor. Chim. Acta*, **15**, 133 (1969).

(17) N. L. Allinger, J. C. Tai, and T. W. Stuart, *Theor. Chim. Acta*, **8**, 101 (1967).

(18) N. L. Allinger and T. W. Stuart, *J. Chem. Phys.*, **47**, 4611 (1967).

10.47 eV (corresponding to the Slater charge, $Z = 3.25$) compared to 11.08 eV used in the earlier version.¹⁴ The former value is close to the value recommended by deBruijn¹⁹ for use in CI calculations (10.50 eV).

The proportionality constant, k , in the formula used for the evaluation of resonance integrals

$$\beta_{12} = 0.5k(I_1 + I_2)S_{12}$$

was recalibrated from the electronic spectra of *cis*-2-butene and benzene. The value used in the present calculations is -0.9768 eV.

The experimental and calculated spectra are given in Table III. This table also includes *p*-xylene as a reference compound.

Table III. Experimental and Calculated Electronic Spectra

Compound	Exptl, ^a nm (eV)	Calcd, nm (eV)
<i>p</i> -Xylene ^b	268 (4.63)	268 (4.63)
	208 (5.97)	207 (5.99)
	188 (6.58)	181 (6.85)
$n = 10^c$	268 (4.63)	268 (4.63)
	218 (5.68)	208 (5.97)
$n = 9^d$	271 (4.57)	180 (6.87)
	219 (5.65)	269 (4.60)
	192 (6.45)	209 (5.93)
$n = 8^d$	275 (4.51)	181 (6.84)
	225 (5.51)	274 (4.52)
	199 (6.24)	212 (5.85)
$n = 7^e$	194 (6.39)	183 (6.78)
	284 (4.36)	181 (6.86)
	232 (5.35)	286 (4.34)
$n = 6^e$		223 (5.56)
	201 (6.18)	(190 (6.53)) ^f
	296 (4.19)	186 (6.68)
$n = 5$	247 (5.02)	305 (4.06)
		245 (5.05)
	205 (6.04)	(207 (5.98)) ^f
	193 (6.41)	
	338 (3.66)	
	292 (4.24)	
	245 (5.06)	
	207 (5.99)	

^a The experimental values are corrected to gas phase by adding 0.12 and 0.19 eV to the second and third transitions, respectively. This is the difference between the vapor phase and solution (*n*-heptane) spectrum of benzene.¹⁰ (The spectra of the [*n*]paracyclophanes were recorded for ethanol solutions, but the positions are not significantly changed when hydrocarbon solvents are used.)

^b L. C. Jones, Jr., and L. W. Taylor, *Anal. Chem.*, **27**, 228 (1955); American Petroleum Institute, Research Project 44, Ultraviolet Absorption Spectral Data, Carnegie Institute of Technology.

^c D. J. Cram and H. V. Daeniker, *J. Amer. Chem. Soc.*, **76**, 2736 (1954). ^d A carboxy derivative, ref 7. ^e A carboxy derivative, ref 5. ^f This transition is only slightly allowed ($f \approx 0.005$) and is not observed. ^g Reference 6.

The calculated first (lowest energy) transition is in all cases in very good agreement with experiment. The observed red shift of this transition as n decreases is also very well accounted for as can be seen in Table IV. The calculated energies for the second and third transitions are generally too high by 0.2-0.3 eV for the second and by 0.3-0.5 eV for the third one. Part of the error in the calculated third transition is, however, also present in the calculated value for the corresponding transition in *p*-xylene (Table III). This error probably reflects a limitation of the π -electron approach in calculations on alkyl-substituted aromatics, as it has been

(19) S. deBruijn, *Theor. Chim. Acta*, **17**, 293 (1970).

Table IV. Shifts in Nanometers Relative to *p*-Xylene

<i>n</i>	First transition		Second transition		Third transition	
	Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
10	0	0	+10	+1		-1
9	+3	+1	+11	+2	+4	0
8	+7	+6	+17	+5	+11	+2
7	+16	+18	+24	+16	+13	+5
6	+28	+37	+39	+38	+17	+12
5		+70		+85		+26

observed in other calculations using different models for the alkyl group.²⁰ The experimental values given in Table III for the two higher energy transitions are also somewhat uncertain since they have been corrected to gas phase in order to make a comparison with theoretical values possible. These corrections can, presently, not be accurately calculated and they can therefore be considered as a first approximation. It should also be noted that by including doubly excited configurations, we are treating the ground state and the singly excited states somewhat unequally.²¹ This unbalance can be corrected by including triply excited configurations

(20) B. Roos, *Acta Chem. Scand.*, **21**, 2318 (1967).

(21) T. W. Stuart and N. L. Allinger, *Theor. Chim. Acta*, **10**, 247 (1968).

which can interact with the singly excited configurations. It has been shown²¹ that the inclusion of triply excited configurations in calculations on benzene and toluene, using the VESCF-CI method, only slightly affects the two lowest energy transitions but lowers the energy of the third by about 0.2 eV. Including triply excited configurations in the present calculations should thus give a somewhat better agreement with experiment. (We are presently not prepared to include triply excited configurations in our calculations.)

It should also be remembered that, due to the diminished validity of the π - σ separation approximation for nonplanar compounds, we cannot expect the same accuracy in π -electron calculations on these compounds as in calculations on planar ones.

The experimental red shifts of the second and third transitions as *n* decreases are qualitatively well reproduced by the calculations (Table IV).

Considering the limitations discussed above, the geometries of the [*n*]paracyclophanes obtained by energy minimization account reasonably well for the electronic transitions of these molecules. The predicted spectrum for the still unknown [5]paracyclophane is given in Table III. It shows the expected shifts to the red of all transitions compared to [6]paracyclophane.

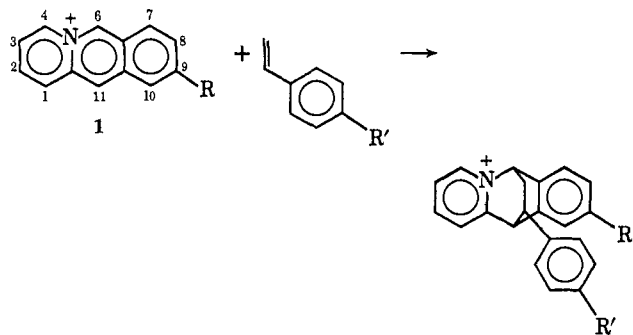
Kinetic Results of a Multiple Substituent Variation in a Polar Cycloaddition. Application of a Frontier Orbital Perturbation Model

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Abstract: Rate constants for cycloaddition of 21 different pairs of 9-substituted acridiziniums and para-substituted styrenes are reported. The rate data can be best fitted to a multiple parameter linear free energy equation proposed by Miller ($\log k = \rho_1\sigma_1 + \rho_2\sigma_2 + q\sigma_1\sigma_2 + c$). The polar cycloaddition is discussed in terms of a frontier orbital perturbation model.

The rates of the cycloaddition reaction of substituted acridiziniums (**1**) with para-substituted styrenes have been shown to be strongly influenced by substituents on



either of the reactants.^{1,2} Thus, rate studies of the

(1) I. J. Westerman and C. K. Bradsher, *J. Org. Chem.*, **36**, 969 (1971).

(2) C. K. Bradsher and J. A. Stone, *J. Org. Chem.*, **34**, 1700 (1969).

addition of 9-substituted acridiziniums with para-substituted styrenes² show that electron releasing groups (*e.g.*, $R' = \text{OCH}_3$) on the styrene and electron withdrawing groups (*e.g.*, $R = \text{NO}_2$) on the acridizinium¹ promote the reaction.

The rates of additions of unsubstituted styrene with 9-substituted acridiziniums are best correlated with the σ_p parameter of the 9 substituent¹ (eq 1).

$$\log k = 1.74\sigma_A - 2.35 \quad (1)$$

The rates of cycloadditions of unsubstituted **1** with para-substituted styrenes correlate well with σ^+ for the styrene substituent (eq 2). σ_A is the σ_p constant³ for a

$$\log k = -0.57\sigma_s^+ - 2.24 \quad (2)$$

substituent at position 9 of acridizinium and σ_s^+ is the Brown-Okamoto constant⁴ for the para-styrene substituent.

(3) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(4) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).