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A THEORETICAL STUDY OF THE STRUCTURES AND ELECTRONIC SPECTRA OF CYCLOBUTADIENE AND DIMETHYLENOCYCLOBUTENE^{1,2}

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Abstract—The structure and UV spectrum of cyclobutadiene have been studied theoretically by a modification of the Pariser–Parr method, which explicitly includes the effect of the sigma system in determining molecular geometry. It was concluded that the ground state is probably a triplet with the geometry of a regular square. The UV spectrum for the actual triplet molecule is predicted to show a strong absorption band at about 363 m μ , and the compound should be colored, probably yellow. The lowest singlet state has a rectangular geometry, and it is predicted to show no allowed transitions above 200 m μ , but because of forbidden transitions at 439 and 487 m μ , should appear red in color.

INTRODUCTION

THE pi system of cyclobutadiene has been subjected to many theoretical investigations, of which the most modern is that reported recently by Dewar and Gleicher,³ which utilized an SCF method.⁴ The method used by Dewar to obtain geometries rests on the assumption that there is a linear relationship between pi bond order and bond length. While such an assumption is certainly very reasonable, it has not been possible to really justify it theoretically or experimentally, although the experimental data on this point also leave much to be desired.*

In the absence of any convincing method for the prediction of the bond lengths in delocalized systems, a method was developed⁶ following earlier suggestions by

TABLE I. CALCULATED BOND LENGTHS (\AA) AND ENERGIES (kcal/mole) OF THE MOST STABLE GEOMETRIES OF REFERENCE COMPOUNDS

	Bond length(s)	E_s	E_t	E_T
Ethylene	1.333	40.62	-243.41	-202.78
Zero-bond order ethylene	1.504	4.55	-95.17	-90.62
Benzene	1.403	129.04	-738.50	-609.46
Butadiene ^a	1.331, 1.470	91.52	-1310.07	-1218.55

* If all bond lengths are kept equal, the minimum of energy is -1214.42 kcal/mole with a bond length of 1.380 \AA .

* The incorporation of a bond-order length relationship into an SCF scheme was considered some years ago.⁵ While this type of procedure enables one to estimate bond lengths in the absence of other data, in 1962 certain key compounds, especially butadiene, possessed experimentally known bond lengths which differed significantly from those predicted with the linear relationship. We were therefore reluctant to use this scheme, although it now appears that it may have been the experimental, rather than the theoretical bond lengths which were in error, at least in the important case of butadiene itself.

Coulson,⁷ in which the sigma system was treated by a classical mechanical method,* while the pi system was treated by a suitable quantum mechanical method, an adaption of the Pariser-Parr method actually having been used.† By this scheme one can calculate the total energy of the molecule as the sum of the energies of the pi and sigma parts. At present one is hampered in the application of this method by the fact that the procedure has not been made automatically adjusting and iterative. One must assume a certain structure, and calculate an energy. Then a somewhat different structure can be assumed, and the energy calculated, and the process can be repeated until one is satisfied that one has a structure sufficiently close the energy minimum. In practice the method has been applied to the determination of gross differences, such as differentiating molecules with alternating long and short bonds from those with equal bond lengths, and it has given satisfactory predictions in this regard. UV spectra have also been reasonably well predicted. Ordinarily the present procedure is too tedious to apply to all possible combinations of bond lengths for a molecule of considerable size or low symmetry. In the case of cyclobutadiene, however, the molecule is sufficiently small and symmetrical that this method can be applied to an exhaustive way.

The synthesis of cyclobutadiene has been as challenging to experimental chemists as an understanding of its electronic system has been to theoreticians. While cyclobutadiene itself has not been isolated and studied in detail, there is strong evidence

* The Westheimer method⁸

† In the earlier paper,⁶ the compression energy of the sigma system was taken as:

$$E_s = 922.5(r - 1.517)^2 \text{ kcal/mole } \text{Å}^2$$

This function was arrived at assuming the natural length for the σ bond was 1.517 Å, and picking the stretching constant so as to give the correct bond length for ethylene. Actually, this procedure is not quite correct, although it gives satisfactory energies for bonds of the lengths ordinarily found in simple olefins and aromatics. For very long bonds, however, it is inadequate. Since we want a double bond with a pi bond order of zero to have a length of about 1.50 Å, we must assign a natural length to the sigma bond so that this will be true. The value 1.517 Å is not the natural length, then, of the sigma bond. While the pi bond order of zero means that the resonance integral (β) is not contributing to a bond shortening, the penetration integrals are still exerting their usual effect, and since this effect is attractive, the double bond will compress to the point where the lowering in energy from the penetration effect is just balanced by the sigma system compression, and the calculated double-bond length will then be too short.

It was therefore decided to derive a new expression of the same form which would predict the correct bond length for ethylene, and predict a bond length of about 1.5 for a double bond of zero pi bond order. The possibility of using a Morse function was considered, but it was decided not to, because of the mathematical complexity of such a function on the one hand, and the fact that adequate results were obtainable using Hooke's law. The expression for compression energy derived is:

$$E_s = 615(r - 1.59)^2 \text{ kcal/mole } \text{Å}^2$$

The value 1.59 Å is the bond length which would result if the pi bond order were zero, in the absence of penetration effects.

This function was checked out by calculating the bond lengths which yield the geometries of minimum energy for ethylene, zero-bond order ethylene, benzene, and butadiene. The results are summarized in Table I. Inspection of the Table shows that the bond length calculated for benzene is too long by 0.006 Å, while the short and long bonds of butadiene have calculated values which are too small by 0.013 and 0.003 Å, respectively. This agreement is regarded as satisfactory, and is illustrative of the accuracy to which we might hope to calculate bond lengths by the present method. The variation of energy with bond length in butadiene (and usually) is very slight. Increasing the length of the short bonds by 0.013 Å, to yield the experimental bond lengths, raises the energy only 0.07 kcal/mole.

for the existence of the molecule as a heavy metal complex, from which the free cyclobutadiene can be generated and subsequently recaptured without change.⁹ Thus it would appear to be only a technical problem to obtain the UV spectrum of the molecule, and the predictions herein are made to assist experimentalists in identifying the material when the time comes.

Considerable discussion has been going on over the years concerning the possibility of the existence of the ground state of cyclobutadiene as a triplet. Experimental evidence on this point is not completely definitive, but tends to suggest that the molecule has a singlet ground state.⁹ On the other hand, tetramethylcyclobutadiene appears likely to have a triplet ground state.⁹

DISCUSSION AND RESULTS

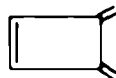
A 4-membered ring contains a rather strained sigma system, and the method which we wished to use for predictions in the case of cyclobutadiene had not previously been demonstrated to be applicable to any compound containing a 4-membered ring. It was deemed advisable, therefore, to first apply the method to the calculation of the properties of a 4-membered ring compound where the accuracy of the predictions could be checked against data to ascertain that the results were valid. We therefore considered the molecule 3,4-dimethylenecyclobutene, which had been prepared earlier and studied experimentally, but on which no theoretical studies had been reported at the time this work was done. Subsequently, a theoretical study on this molecule was reported by Brown.¹⁰

The best experimental spectrum of 3,4-dimethylenecyclobutene available is that reported by Heffernan.¹¹ Unfortunately, the exact geometry of the molecule has not been reported. This would be a more incisive test of the accuracy of the calculations, as some uncertainty exists as to the value of the appropriate stretching constant for a sigma bond which is so highly deformed.

For dimethylenecyclobutene, there seemed to be two general types of structures which were reasonable. One of these would have all of the bond lengths approximately equal, and approximately 1.397 Å (structure E). The other possibility, which seems intuitively more reasonable, would be that the bonds would alternate in length (as in the Kekulé structure, A) and might be expected to have values on the



E



A

order of 1.35 and 1.47 Å for bonds written as double and single respectively. These are close to the values that are obtained using a bond-order, bond-length relationship, so that we actually used the latter to obtain the bond lengths given in the Appendix. The pi energy was found to be lower for A than for E by 3.0 kcal/mole, while the sigma energy (compression energy) was 4.6 kcal/mole lower. Thus it is predicted that A is of lower energy than E by 7.6 kcal/mole.

The calculation on a structure with equivalent bond lengths of 1.424 Å was also carried out (E'). Here the total energy was found to be higher by 1.7 kcal/mole relative to E.

The UV spectra calculated for structures A and E using a singly-excited configuration interaction treatment are presented in Table 2, along with the experimental values. It should be emphasized that there are no available parameters to adjust in the calculation of spectra in this paper, all of the numerical quantities needed are available from previous work.^{1,6} The spectrum predicted for structure A is in

TABLE 2. THE ELECTRONIC SPECTRUM OF 2,3-DIMETHYLENOCYCLOBUTENE

Calculated								Experimental ¹¹	
Singly-excited configurations ⁶				Doubly-excited configurations				$\lambda(\text{m}\mu)$	$\log \epsilon$
E		A		E		A			
$\lambda(\text{m}\mu)$	(f)	$\lambda(\text{m}\mu)$	(f)	$\lambda(\text{m}\mu)$	(f)	$\lambda(\text{m}\mu)$	(f)		
303	(0-11)	269	(0-10)	303	(0-00)	256	(0-00)	—	—
295	(0-00)	262	(0-00)	276	(0-13)	238	(0-17)	240	4.2
208	(0-93)	200	(0-92)	216	(0-06)	194	(0-60)	205	5.0
199	(0-90)	197	(0-79)	207	(0-11)	188	(0-10)		
163	(0-11)	157	(0-09)	202	(0-64)	186	(0-54)		
				193	(0-61)	174	(0-17)		
				162	(0-13)	151	(0-06)		

fair agreement with that observed experimentally, while that of E is quite different. It has been noted previously⁶ that when the doubly-excited configurations are included in the configuration interaction treatment, any change in the calculated spectrum is usually an improvement. When this type of calculation (VESCFC) was carried out for dimethylenecyclobutene, the spectrum calculated for A was in good agreement with experiment. Hence, it was concluded that the strain present in the 4-membered ring exerts no anomalous effect on the ultraviolet spectrum, and one might therefore reasonably hope to apply this method to cyclobutadiene with some degree of confidence.

The same general methods described above were next used to study separately the two general possible geometric structures for cyclobutadiene, R, a rectangular form, and S, the square form.



R



S

As a starting point for a study of the rectangular form of the molecule, we chose that geometry suggested by Dewar which has alternating double and single bonds with bond lengths of 1.338 Å and 1.514 Å respectively. The pi system was treated by the usual method, with configuration interaction including only the singly-excited states, and including penetration integrals. The energy of the sigma system was computed as previously and added to that of the pi system. The total calculated electronic energy for that particular geometry was found for both the singlet and for the triplet. The single bonds were then shortened to a length of 1.510 Å, and the

calculations were repeated. (Since the energy of the lowest singlet state was always below that of the lowest triplet state for (R), the following discussion is concerned with the singlet states only.) In this case the total energy had gone up slightly. The single and double bond lengths were then repeatedly adjusted by a few thousandths of an Å each way, and the calculation was again repeated several times, until it was established that geometry corresponding to the energy minimum had been located. The bond lengths for this geometry were 1.334 and 1.518 Å. The ultraviolet spectrum that would be shown by this structure was also calculated by the previously discussed methods. The geometric data are presented in Table 3, and the spectroscopic data in Table 4.

TABLE 3. CALCULATED GEOMETRIES AND ENERGIES FOR DIFFERENT POSSIBLE ELECTRONIC STRUCTURES FOR CYCLOBUTADIENE

	R_{12}	R_{23}	E_{σ}	Singlet E_{π}	Triplet E_{π}	$E_{\text{Total}}^{\text{Singlet}}$	$E_{\text{Total}}^{\text{Triplet}}$
(S)	1.424	1.424	67.8	-1276.6	-1299.4	-1208.8	-1231.6
(R)	1.334	1.518	87.0	-1312.5	-1307.7	-1225.5	-1220.7

TABLE 4. THE CALCULATED ELECTRONIC SPECTRA FOR CYCLOBUTADIENE IN THE SINGLET AND TRIPLET STATES

Singlet (R)				Triplet (S)			
Singly-excited configurations		Doubly-excited configurations		Singly-excited configurations		Doubly-excited configurations	
λ_{mp}	(f)	λ_{mp}	(f)	λ_{mp}	(f)	λ_{mp}	(f)
589	0.0	487	0.0	305	0.4	387	0.01
209	0.0	439	0.0	235	0.4	363	0.16
156	1.2	192	0.2			171	
						168	

If we first examine Table 3, we note that for the singlet the energy (E_7^S) is much lower for the rectangular form than it is for the square form. The triplet, on the other hand, is more stable in the square form (E_7^T). Perhaps the most interesting result is that the square triplet is predicted to be 6.1 kcal/mole more stable than the rectangular singlet, however this is not a very large energy difference for a calculation of this type, and must be accepted with some reserve. It may well be that the single-triplet stability relationship depends on the circumstances; the calculation here is, of course, for the isolated molecule in the gas phase. It seems quite possible that substituted cyclobutadienes may be found with either multiplicity having the lower ground-state energy.

The UV spectra were studied by the methods described, and the results are summarized in Table 4. For the rectangular singlet, no allowed transitions are predicted in the easily observable region. Forbidden transitions are predicted at 487 and 439 m μ for the calculation regarded as the more reliable (including doubly-excited configurations). These should be observable with low extinction coefficients (probably $\epsilon = 10-200$), and should cause the compound in this state to be colored, probably red.

Because of the degeneracy present in the system (S), the T_{2234} configuration which is formally a doubly-excited configuration is actually degenerate with T_{24} , and in fact the double excitation is really a result of nomenclature, as to reach either of these two states from T_{23} , a single excitation of an electron is required, from 3 to 4 in one case, and from 2 to 4 in the other. Since 2 and 3 are degenerate, it would seem that limiting the configuration interaction to a consideration of only singly-excited configurations (according to nomenclature) is not really legitimate. In this case, the configuration interaction between T_{24} and T_{13} causes these levels to be split further apart, so that the transition to the lower one was shifted out to 360 $m\mu$, while that to the higher one was pushed far down into the unobservable ultraviolet region. Another pair of transitions from the formally doubly-excited but degenerate set of states occurs in addition, and after configuration interaction (because some of these configurations interact with other doubly-excited configurations), the transitions are not degenerate. In this case, only one strongly allowed transition was predicted in the observable region at 380 $m\mu$.

Because of the degeneracy, the square cyclobutadiene triplet is an unusual case, in that while termination of the configuration interaction with the singly-excited states is a clear-cut concept ordinarily, in this case it is more in line with the conventional treatment for the prediction of spectra to include the doubly-excited configurations here. Hence, the spectra which we predict will be observed for the molecule in the triplet state should show an absorption band about 360 $m\mu$ with an extinction coefficient of a few thousand. The compound in this state should therefore be colored, probably yellow, from the tail absorption of this band.

REFERENCES

- ¹ Paper XV, N. L. Allinger, J. C. Tai and T. W. Stuart, *Theoret. Chim. Acta*, **8**, 101 (1967).
- ² This research was supported by grant GP 4290 from the National Science Foundation.
- ³ M. J. S. Dewar and J. Gleicher, *J. Am. Chem. Soc.* **87**, 3255 (1965).
- ⁴ For a summary of earlier work, and pertinent Refs. see Ref. 3, and also S. Shida, *Bull. Chem. Soc., Japan* **27**, 243 (1954); S. Shida and Z. Kuri, *J. Chem. Soc., Japan (Pure Chem. Section)* **76**, 322 (1955); and D. P. Craig, *Proc. Roy. Soc.* **202A**, 498 (1950).
- ⁵ R. B. Hermann, *A Theoretical Investigation of the Extension of the Hückel Rule to certain Heterocyclic Systems*, a dissertation submitted at Wayne State University, March (1962).
- ⁶ W. Haugen and M. Traetteberg, *Acta Chem Scand* **20**, 1726 (1966).
- ⁷ N. L. Allinger, M. A. Miller, L. W. Chow, R. A. Ford and J. C. Graham, *J. Am. Chem. Soc.* **87**, 3430 (1965).
- ⁸ C. A. Coulson, *Tetrahedron* **12**, 193 (1961).
- ⁹ E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis*, p. 446. Interscience Division of Wiley, New York (1965).
- ¹⁰ L. Watts, J. D. Fitzpatrick and R. Petit, *J. Am. Chem. Soc.* **89**, 3254 (1965); P. S. Skell, *Ibid.* **86**, 2530 (1964).
- ¹¹ R. D. Brown and F. R. Burden, *Chem. Comm.* **14**, 448 (1966).
- ¹² M. L. Heffernan and A. J. Jones, *Ibid.* 120 (1966); see also A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.* 332 (1961). The authors are indebted to Dr. Heffernan for a copy of the actual spectrum.