Tetrahedron. Vol 27, pp 2877 to 2883. Pergamon Press 1971. Printed in Great Britain

FIRST- VS. SECOND-ORDER BOND FIXATION AND VALENCE ISOMERIZATION IN DONOR–ACCEPTOR-SUBSTITUTED CYCLOBUTADIENES

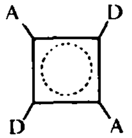
R. WEISS[*] and J. N. MURRELL

School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ

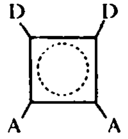
(*Received in the UK* 3 *November* 1970; *Accepted for publication* 14 *December* 1970)

Abstract—On the basis of HMO-, SCF-π- and Mindo/2 ($\sigma + \pi$) calculations it is predicted that 'push-pull' (tetra-)substituted cyclobutadienes will have a tendency to distort from a square to a rectangular structure. Depending on whether the 'push-pull' substituent pairs are arranged in a parallel or crosswise manner this particular type of bond fixation is of first or second order resp. The calculations also predict comparable heats of formation for the two isomer cyclobutadiene types—in contrast to a rule recently formulated by R. Hoffmann. An explanation for this discrepancy is given. Attention is drawn to the different shape of the potential curves of valence isomerization in the two cyclobutadiene types.

IN A recent communication[1] R. Hoffmann predicted different thermodynamic stabilities for donor-acceptor substituted cyclobutadienes of type *A* and *B*:



A



B

He assigned a greater stability to type **A** on the basis of a greater, symmetry-favoured splitting of the frontier orbital pair which is degenerate in square (triplet) cyclobutadiene (CBD) itself.

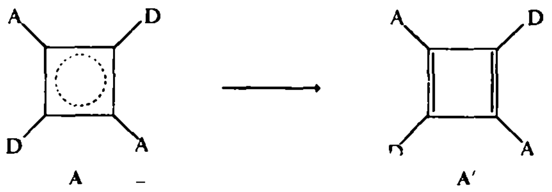
In this communication we show that Hoffman's conclusion is untenable because it was based on the assumption that the bond lengths of the four-membered ring remain equal on substitution. Square cyclobutadiene is susceptible to a Jahn–Teller distortion because of its orbital degeneracy and experimental as well as theoretical evidence indicates that CBD in its groundstate is rectangular.[2]

Substitution in the pattern of either **A** or **B** will remove the orbital degeneracy associated with the square CBD ring but it is not *a priori* clear whether this will also remove the tendency to distort to a rectangular structure altogether. The distortion **A** → **A′** may be called a pseudo Jahn–Teller effect, or, in the terminology of Binsch, Heilbronner and Murrell,[3] second order bond fixation. There are clearly two equivalent (or, if the nature of the substituents does not allow full D_{2h}-symmetry, nearly equivalent) structures for this distorted molecule.

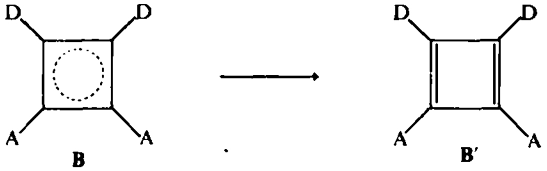
For compounds of type **B** on the other hand there is just one low energy structure

---

[*] Nato-fellow 1969/70. Now at: Institut für Organische Chemie der Universität München, 8 München 2, Karlstr. 23



(**B′**), resulting from first-order bond fixation. This is not first-order in the Jahn–Teller sense, but according to the definition of reference[3] a distortion which does not lower the symmetry and is associated with the familiar bond order-bond length relationship of π-electron theory:

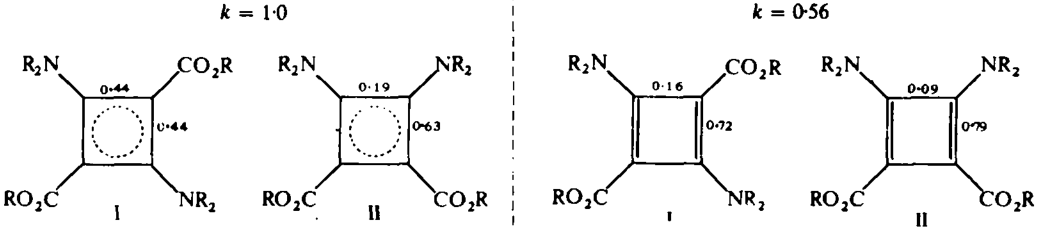


Our calculations show that one may expect both types of distortion to occur and that the corresponding energy gain for CBD **B** is appreciably larger than that for CBD **A** and compensates for its comparatively smaller energy stabilization resulting from the substituent perturbation of the regular 4-membered ring.

The following calculations support our contention. They have been made with the substituents D = NR_2, A = COOR, because the first stable CBD of type **A** with these substituents has recently been prepared.[4]

Hückel Calculations

Using standard Hückel parameters we have made calculations on the basis of regular 4-membered rings, and for rectangular rings with the ratio $k = \beta_s/\beta_d = 0{\cdot}56$ for the resonance integrals of the double and single bonds. This ratio has been found to be qualitatively satisfactory as a bond alternation parameter.[5] The results for the two representatives I and II of the CBD types **A** and **B** are shown below:



$k = 1{\cdot}0$, I	$k = 1{\cdot}0$, II	$k = 0{\cdot}56$, I	$k = 0{\cdot}56$, II
$E_\pi = 27{\cdot}82\,\beta$	$E_\pi = 27{\cdot}52\,\beta$	$E_\pi = 28{\cdot}24\,\beta$	$E_\pi = 28{\cdot}22\,\beta$
$\Delta = 0{\cdot}903\,\beta$	$\Delta = 0{\cdot}250\,\beta$	$\Delta = 1{\cdot}12\,\beta$	$\Delta = 0{\cdot}870\,\beta$

It is obvious from the bond orders in the CBD-ring that for $k = 1{\cdot}0$ II exhibits a strong tendency for first order bond fixation, whereas I—due to its higher symmetry (pseudo-D_{2h} as opposed to pseudo-C_{2v})—does not. If then one allows these molecules to distort according to **A** → **A**′ and **B** → **B**′ one finds that both I and II profit in π-energy from this process but II to a substantially higher degree. As a result the π-energies of the two isomers become almost identical for the assumed degree of bond fixation. Furthermore, the splitting Δ of the frontier orbitals in II is much more sensitive towards this particular distortion than in I—with full double bond localization the size of Δ becomes comparable.

SCF Calculations

One may regard the HMO results as a qualitative hint that both CBD types have a tendency for double bond fixation. In order to substantiate this it seemed desirable to resort to a reliable SCF-procedure which ideally should also take into account the changes in σ-energy with distortion. This requirement is met by a recent variant of Pople's SCF-procedure, developed by Dewar and Harget[6] which has been parameterized to reproduce experimental heats of formation for compounds containing conjugated C, N and O atoms. In the program available for these calculations the bond lengths are automatically adjusted to be self-consistent to the bond orders ('varied r'-calculation). The results obtained with this type of calculation are given in Table I. If one initiates the iterations with the square geometries I and II (corresponding to fully delocalized singlet structures) one finds that after convergence has been reached the final geometries correspond to structures Ia and IIa with fully localized double bonds in the CBD ring. The same energies and geometries were obtained with structures *Ia* and *IIa* as *starting* geometries. Structure IIb is metastable with respect to IIa and represents a local energy minimum which was found by starting the calculation with a corresponding rectangular geometry.

II distorts in very much the same way as indicated by HMO-bond orders—therefore one here has a typical case of first order bond fixation. I has no tendency for first order bond fixation within the HMO-approximations. Except for a minor difference in bond orders for the two different ring bonds (caused by the asymmetry of the carboxyl-groups) this will still be true for any SCF-procedure. Therefore the reduction of (pseudo-) symmetry of I from D_2h to C_2h must be effected by second order bond fixation. In contrast to first order bond fixation second order bond fixation can reduce the symmetry of a molecule (c.a.).

The remarkable feature about the results in Table I is that Ia is only some 2·3 kcals. less stable than Ia with the splitting of the corresponding frontier orbitals being virtually identical. This is largely in accordance with simple HMO-considerations discussed above, and very much in contrast to the predictions of ref. 1. The situation is illustrated in Diagram I. In chemical language these results can be plausibly interpreted in terms of weakly interacting *cis*-aminoacrylester-units—whereby for the groundstate energies of Ia and IIa it is of little consequence whether these units are linked in a head-to-head or head-to-tail fashion. The thermodynamic data suggest that *IIa* like *Ia* should be an isolable compound. The fact that 'varied-r' calculations for I and II converge to solutions which correspond to the distorted structures Ia and IIa indicates that I and II do not even represent a metastable state of these molecules but rather the transition state of the valence isomerizations Ia ⇌ Ib and IIa ⇌ IIb.

TABLE 1. SCF-CALCULATIONS ON DONOR–ACCEPTOR SUBSTITUTED CYCLOBUTADIENES

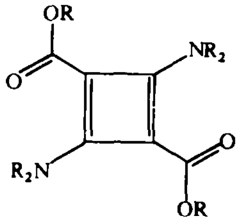
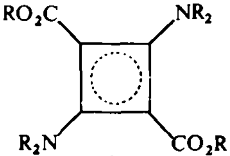
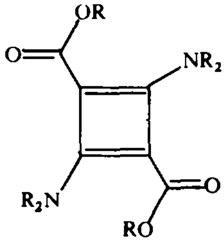
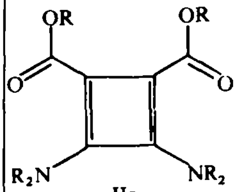
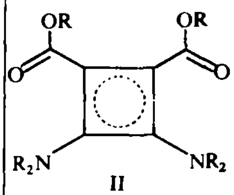
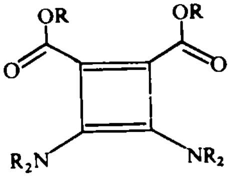
Compound*	Heat of formation† (closed shell) [EV]	Heat of formation (open shell) [EV]
 Ia	−82·51 $\begin{Bmatrix}0{\cdot}496\\8{\cdot}397\end{Bmatrix}$ ↑	? ↓
 I	?	−82·30 $\begin{Bmatrix}4{\cdot}033\\4{\cdot}929\end{Bmatrix}$ ↑
 Ib	−82·47 $\begin{Bmatrix}0{\cdot}525\\8{\cdot}395\end{Bmatrix}$	?
 IIa	−82·41 $\begin{Bmatrix}0{\cdot}526\\8{\cdot}356\end{Bmatrix}$ ↑	? ↓
 II	?	−82·34 $\begin{Bmatrix}4{\cdot}33\\4{\cdot}38\end{Bmatrix}$ ↑

TABLE 1—*cont.*

Compound*	Heat of formation† (closed shell) [EV]	Heat of formation (open shell) [EV]
 IIb	−82·18 {0·844 8·028}	↑ ?

* Only minimum energy conformations of the estergroups are shown

† Numbers in brackets correspond to SCF-energies of frontier orbitals.

In this context it would be of interest to know the energy difference between I and IIa as well as II and IIa to have a *rough* estimate of the activation barrier of these valence isomerizations.

In an SCF-procedure the energies of structures like I and II cannot be obtained because there are not enough symmetry elements which would enforce the equality of bond orders in the CBD-ring (and therefore prevent the molecule from distorting in the course of the iterative procedure). This is in fact quite generally true for all subst. cyclobutadienes of type **B**, as the distorted and undistorted structures both belong to the same symmetry group and one automatically calculates the lowest energy structure.

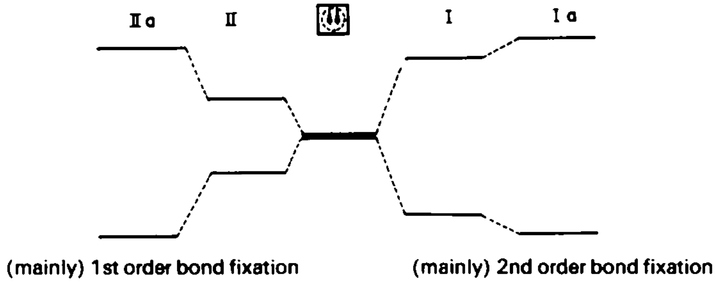
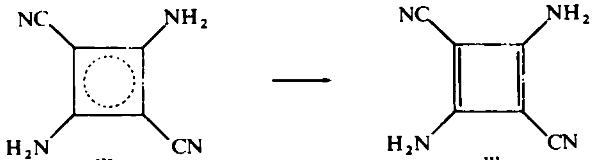


DIAGRAM I. THE SPLITTING OF THE FRONTIER ORBITALS OF SQUARE CBD UPON SUBSTITUTION AND SUBSEQUENT DISTORTION

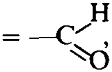
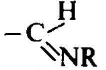
For cyclobutadienes of type **A**, however, a hypothetical compound of structure III with strict D_{2h}-symmetry may serve as model case to estimate the energy difference between the localized and delocalized singlet structures:



III IIIa

Using the Mindo/2—all valence electron method[7] and standard bond lengths the gain in energy due to second order bond fixation in going from III to IIIa was calculated to be about 3 kcals mole^{-1}. In addition, the energy was found to decrease smoothly along a reaction coordinate from III to IIIa so that III lies on an energy maximum between the equivalent valence isomers of structure IIIa. This result means that III—like I—and naturally II—is not even a metastable species. The smallness of the calculated activation energy makes it likely that there is rapid bond shifting in cyclobutadienes of type **A** even at low temperature. This is consistent with the fact that no splitting of the NMR N-alkyl-signals of a CBD of type **A** (D = $N(C_2H_5)_2$, Y = $CO_2C_2H_5$) was observed even at −40°C whereas in a corresponding amino-acrylester such a splitting is known to occur at 0°C already.[8]

At present this particular CBD is being investigated by X-ray.[9] It will be very interesting to see whether there will be any indications of bond fixation in the solid phase, although it seems more likely that only an average structure (square) will be recorded.

The energetical effects discussed above and the different phenomena of bond fixation are not restricted to the particular types of substituents considered so far, that is: A = CO_2R, CN and D = NR_2. Further sample calculations with A =  $-\mathrm{C}(\mathrm{H}){=}\mathrm{O}$,  $-\mathrm{C}(\mathrm{H}){=}\mathrm{NR}$ and D = OR showed that SCF-calculations quite generally predict first and second order bond fixation for all cyclobutadienes of chemical interest which are substituted according to pattern **A** or **B**. The numerical details are very similar to the ones in Table I and need not be discussed further.

Although the energy difference between the localized and delocalized CBD structures in general, and in particular between IIa and II (as a crude measure of the activation energy of the process IIa $\rightleftharpoons$ IIb) could not be obtained with the methods of calculation used, it is qualitatively clear that transition state II is at distinctly higher energy than I. One only has to realize that Hoffman's rule about the modes of stabilization of subst. cyclobutadienes is—in a one-electron scheme—rather a rule about the energy levels of transition states in the valence isomerizations of these molecules. In a many-electron scheme one has in addition in II unfavourable core—core and electron-electron repulsions, not present to that extent in I, which are caused by the charges imposed on the ring by the substituents (cf. diagram II). If one relaxes the

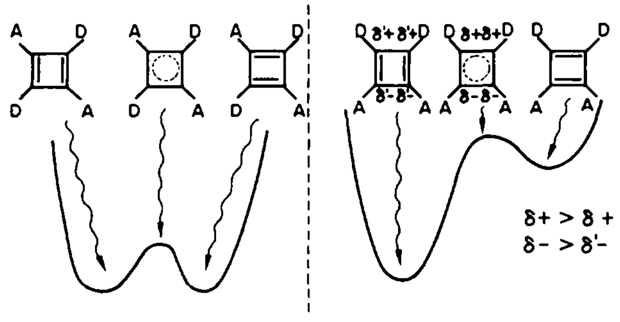


DIAGRAM II. POTENTIAL CURVES FOR VALENCE ISOMERIZATION IN CYCLOBUTADIENES OF TYPE **A** AND **B** geometry of II according to the requirements of first order bond fixation these unfavourable interactions are relieved. This fact should accentuate the tendency of bond fixation.

Guided by these considerations and on the basis of the numerical results discussed before, one can attempt to formulate the qualitative shape of the corresponding potential curves as shown in Diagram II in a generalized manner.

It is important to realize that this scheme is only valid for closed shell structures and that it may have to be modified by the possible intermediacy of square triplet structures. A look at Table I shows that there are indeed square diradical structures of low energy, but as the SCF-π-program used only yields energies corresponding to the centre of gravity of the square singlet and triplet diradical structures the matter was not followed up.

Acknowledgement—Helpful discussions with A. Harget are gratefully acknowledged. This work was supported by a Nato-grant of the DAAD (Bonn, W. Germany) to R.W.

REFERENCES

[1] R. Hoffmann, *Chem. Comm.* 241 (1969)
[2] M. J. S. Dewar, M. C. Kohn and N. Trinajstić, *J. Am. Chem. Soc.* in press
[3] G. Binsch, E. Heilbronner and J. N. Murell, *Mol. Phys.* **11**, 305 (1966)
[4] R. Gompper and G. Seybold, *Angew. Chem.* **80**, 804 (1968)
[5] R. Weiss and J. N. Murrell, *Tetrahedron*, **25**, 1131 (1970)
[6] M. J. S. Dewar, A. Harget and N. Trinajstić, *J. Am. Chem. Soc.* **91**, 6321 (1969)
[7] M. J. S. Dewar and E. Haselbach, *Ibid.* **92**, 590 (1970)
[8] G. Seybold, Ph.D. Thesis, Universität München 1969
[9] G. Seybold, private communication.