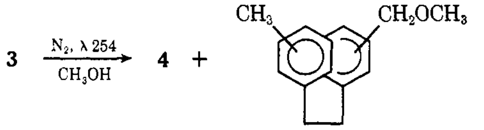
Irradiation (quartz U tube, low-pressure mercury arc of *ca.* 2 W, 86% at 254 nm) of a cyclohexane solution (10^{-4} *M*) of [2.2]metaparacyclophane (**3**) under nitrogen for 4 hr gave a mixture of starting material (50% recovery) and [2.2]metacyclophane (**4**): yield 42% (based on consumed **3**); mp 132–133°, undepressed by admixture with an authentic sample;[8] nmr spectrum indistinguishable from that of the authentic sample.[8] This conversion, coupled with the isomerization (44% yield)[4] of commercially available[9] [2.2]paracyclophane to [2.2]metaparacyclophane, provides a simple route to [2.2]metacyclophane.

When submitted to the above irradiation conditions for 8 hr, (−)-**2** (maximum rotation) gave 27% recovered (−)-**2** that was 86% racemized and a mixture of isomeric methyl[2.2]metacyclophanes[2] (**5**). When **3** was submitted to the same radiative conditions in methanol for 4 hr, a 46% yield of **4** was produced as well as a 25% yield of an open-chain ether,[2] **9**. These facts suggest that like the [2.2]paracyclophane, the [2.2]metaparacyclophane system[3b] undergoes a photolytic benzyl–benzyl bond cleavage reaction to give a zwitterion-like intermediate which, after conformational adjustments, either ring closes back to **3** or gives methanolysis product. However, unlike [2.2]paracyclophane, [2.2]-metaparacyclophane (**3**) photolytically ring contracts to a less strained cyclophane (**4**) probably by a benzvalene or prismane route.[10a] Others have noted considerable differences in the photolytic behavior of the position isomers of dialkylated benzenes, the para isomers usually being the least reactive.[10b,c] The reduction in strain energy of 10 kcal/mol in passing from **3** to **4**[11] probably contributes to the occurrence of this reaction, although an 8-kcal/mol release of strain energy[11] is potentially available for the photolytically unobserved conversion of [2.2]paracyclophane to [2.2]metaparacyclophane.[3b]



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[11] C. Shieh, D. C. McNally and R. H. Boyd, *Tetrahedron*, **25**, 3653 (1969).

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Bond Index Interpretation of Valence Isomerization

Sir:

In most cases it has been assumed that photochemical reactions start from the first excited state as a consequence of its longer lifetime. Recently, however, van der Lugt and Oosterhoff have emphasized the possibility that after excitation of a molecule into a higher excited state the reaction originates from this state before radiationless conversion to the first excited state occurs.[1]

Although extensive studies of photochemical reactions using monochromatic light are required to determine which of the excited states is involved, we can approach this problem by a simple method, at least in the case of valence isomerization reactions. In this report we describe an interpretation of Wiberg's bond index[2,3] which partitions the charge into various valence-bond (VB) structures for excited states.

The bond index in an excited state is defined as the square of the bond order in that state

$$W_{ab}^* = (P_{ab}^*)^2 \tag{1}$$

where the asterisk labels the excited state and a and b label atomic orbitals in LCAO expansion. Let us suppose that a molecule is in the excited state corresponding to the one-electron excitation $\psi_j \rightarrow \psi_k$. If we sum W_{ab}^* over all atomic orbitals b, we obtain

$$\begin{aligned}\sum_{b} W_{ab}^* &= 2q_a - 3C_{ja}^2 + C_{ka}^2 \\ &= 2q_a^* - (C_{ja}^2 + C_{ka}^2) \qquad (2)\end{aligned}$$

where q_a is the charge density of the ground state and q_a^* is that of the excited state. Equation 2 may be modified as follows

$$q_a^* - {}^1/_2(C_{ja}^2 + C_{ka}^2) - {}^1/_2W_{aa}^* = {}^1/_2\sum(K)\sum(\text{b in } B_K)W_{ab}^* \tag{3}$$

We define the term $[q_a^* - {}^1/_2(C_{ja}^2 + C_{ka}^2) - {}^1/_2W_{aa}^*]$ as the active charge in the excited state, A_a^*.

From the partitioning of active charge into VB structures we observe that the relative weight of a certain VB structure changes greatly depending on the electronic state. Consider the π system in butadiene. The active charges in the ground state are $(A_1, A_2, A_3, A_4) = (0.5, 0.5, 0.5, 0.5)$, in the configuration $(\psi_2 \rightarrow \psi_3)$, $(A_1^*, A_2^*, A_3^*, A_4^*) = (0.138, 0.362, 0.362, 0.138)$. The active charges of *cis*- and *trans*-butadiene are partitioned in various VB structures (Chart I,[4] where the superscript $(j \rightarrow k)$ labels the one-electron excitation $\psi_j \rightarrow \psi_k$). The bond index, W_{ab}, is considered as the charge in orbital a which participates in an a–b bond. If a certain electronic state of a molecule has little charge in a region where a new bond is formed during valence isomerization, the state is considered energetically unfavorable for the isomerization to occur, since the nuclear configuration of the molecule must be changed much to acquire charge in that region. Therefore, we can assume that photochemical valence isomerization occurs from the excited state which most resembles the structure of the product in the VB structure.

The eigenvalues corresponding to the first and second excited states for singly excited singlet configurations of *trans*-butadiene are −71.283 and −70.381 eV, re-

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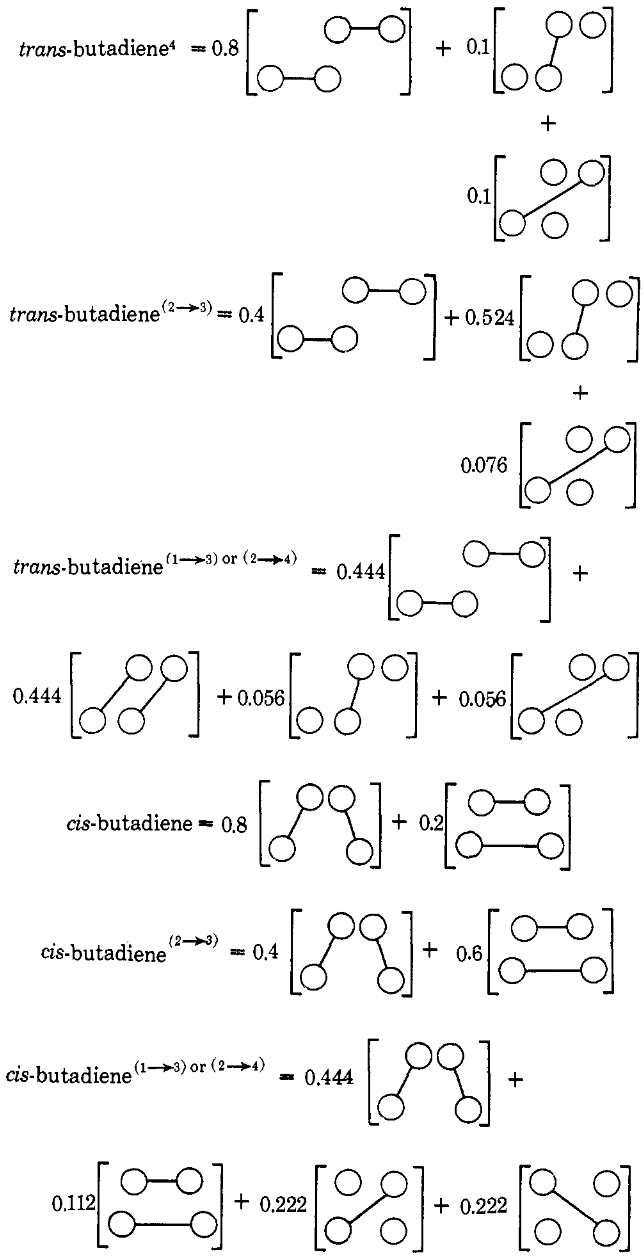
[1] W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

[2] K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

[3] C. Trindle, *J. Amer. Chem. Soc.*, **91**, 219 (1969).

[4] Trindle's treatment of ref 3 gives active charges slightly different from ours due to his use of CNDO SCF wave functions.

Chart I



spectively,[5] and the corresponding CI wave functions are

$$^1\Psi_{\mathrm{CI}}{}^{\mathrm{first}} = 0.992\psi_{\mathrm{II}} + 0.135\psi_{\mathrm{V}}$$

$$^1\Psi_{\mathrm{CI}}{}^{\mathrm{second}} = 0.707\psi_{\mathrm{III}} + 0.707\psi_{\mathrm{IV}}$$

where

$$\psi_{\mathrm{II}} = (1/\sqrt{4})(1/\sqrt{2})(\det\{\psi_1\bar{\psi}_1\psi_2\bar{\psi}_3\} - \det\{\psi_1\bar{\psi}_1\bar{\psi}_2\psi_3\})$$

$$\psi_{\mathrm{III}} = (1/\sqrt{4})(1/\sqrt{2})(\det\{\psi_1\bar{\psi}_1\psi_2\bar{\psi}_4\} - \det\{\psi_1\bar{\psi}_1\bar{\psi}_2\psi_4\})$$

$$\psi_{\mathrm{IV}} = (1/\sqrt{4})(1/\sqrt{2})(\det\{\psi_1\psi_2\bar{\psi}_2\bar{\psi}_3\} - \det\{\bar{\psi}_1\psi_2\bar{\psi}_2\psi_3\})$$

$$\psi_{\mathrm{V}} = (1/\sqrt{4})(1/\sqrt{2})(\det\{\psi_1\psi_2\bar{\psi}_2\bar{\psi}_4\} - \det\{\bar{\psi}_1\psi_2\bar{\psi}_2\psi_4\})$$

CI calculations show us that the first excited state is composed largely of the ψ_{II} configuration and the second excited state of the ψ_{III} and ψ_{IV} configurations. With this analysis and the above assumption, we may say that cyclobutene formation is favored from the first excited state of *cis*-butadiene, and bicyclobutane formation is favored from the second excited state of *trans*-butadiene.

According to selection rules,[6] *trans*-butadiene cannot reach the second excited state. However, it is reasonable to consider that *trans*-butadiene reaches this state from the vibrationally excited ground state[7] that is formed by internal conversion from the excited singlet state, since the calculated energy difference between the first and second excited states is very small. The probability of this process, however, should be very small. Therefore, we can explain the experimental results that bicyclobutane is produced in much smaller amount than cyclobutene in spite of the fact that in equilibrium butadiene assumes largely the *s*-trans conformation, and that the yield of bicyclobutane is decreased by an increase in pressure.[8,9]

Correlation diagrams based on orbital and symmetry[10] gave the same results as bond index analyses. In this respect Trindle's method of mapping analysis[11] is considered to be useful for studying open-shell-system reactions. Full details of work on various systems are now in preparation.

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Selective Oxidation of Unactivated Methylene Groups by Reagent–Substrate Orientation in Mixed Complexes

Sir:

Previous reports from our laboratory have described the development of a new synthetic procedure, remote oxidation, and its application to the functionalization of straight-chain[1] or steroid substrates.[2] The process involves attachment of a rigid ketonic reagent to the substrate, followed by irradiation. This generates an excited carbonyl group in the reagent, which then attacks a substrate C–H bond remote from the point of attachment. In some cases this is followed by abstraction of a second hydrogen from the substrate,[2] with the overall result being direct introduction of a double bond in a selective fashion into a particular position of the substrate. In other cases,[1,2] the intermediate diradical couples to form a new carbon–carbon bond; straightforward chemical processes can be used to convert this to a product with a new carbonyl group selectively introduced into the substrate,[1,2]

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