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ACYCLIC AROMATICITY. TRIMETHYLENEMETHANE DIANION

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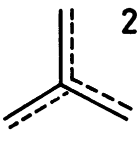
The extent of electron delocalization in acyclic π-conjugated systems such as the dianions of trimethylenemethane and butadiene is shown to be determined by the orbital phase continuity-discontinuity properties.

Certain cross-conjugated species such as dianion 1 was suggested$^{1)}$ to possess a novel aromatic character, even though the cojugation is acyclic. Recently a few experimental verifications appeared.$^{2,3)}$ We will disclose *cyclic* orbital interaction in *acyclic* conjugation by employing the many-system electron delocalization theory,$^{4-7)}$ and apply the orbital phase continuity requirements for electron delocalization to the dianions of trimethylenemethane (1) and butadiene (2).



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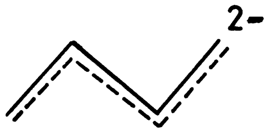

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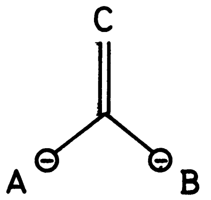

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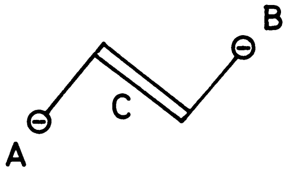

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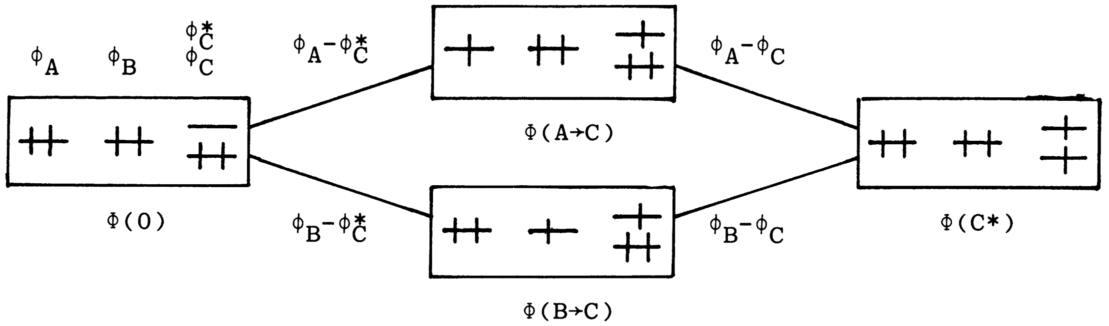
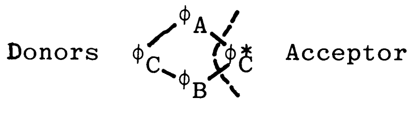
Trimethylenemethane dianion 1 is considered to be a π-conjugated system where two anion centers (A, B) and a double bond (C) interact with one another (3). Butadiene dianion 2 has the identical subsystems which, however, lie in the different relative positions (4). The electronic structure, $\Phi(0)$, corresponding to the Kekule structure 3, is shown in Scheme. There are two one-electron transferred configurations, $\Phi(A \rightarrow C)$ and $\Phi(B \rightarrow C)$, and a one-electron locally-excited configuration $\Phi(C^*)$. The configuration interaction between $\Phi(0)$ and $\Phi(A \rightarrow C)$ involves the orbital interaction between ϕ_A and ϕ_C^*. The $\Phi(0)$-$\Phi(B \rightarrow C)$ interaction involves the ϕ_B-ϕ_C^* interaction. The $\Phi(A \rightarrow C)$-$\Phi(C^*)$ interaction involves the ϕ_A-ϕ_C interaction. The $\Phi(B \rightarrow C)$-$\Phi(C^*)$ interaction involves the ϕ_B-ϕ_C interaction. As a result, the orbital interaction among ϕ_A, ϕ_B, ϕ_C, and ϕ_C^* is *cyclic* (5). In addition, the electron-donating (occupied) orbitals are on one side of the circle with the electron-accepting (unoccupied) orbital on the other (5). Therefore, the delocalization is under the control of the orbital phase continuity-discontinuity properties.$^{5)}$ The orbital phase continuity requirements$^{4)}$ are: (1) the donating orbitals out of phase, (2) the donating and accepting orbitals

Scheme





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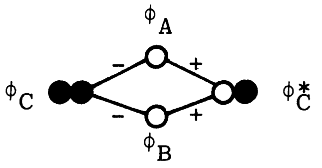

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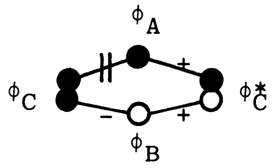

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in phase, and (3) the accepting orbitals in phase. The orbitals in cyclic array 5 meet the requirements (6). Trimethylenemethane dianion 1 is then electron-delocalizing, or aromatic. By contrast, the cyclic orbital interaction among ϕ_A, ϕ_B, ϕ_C, and ϕ_C^* dissatisfies the phase continuity requirements (7). The electron delocaliztion is disfavored. The resulting prediction that 1 is more stable than 2 is consistent with the experimental results.$^{3)}$

The one-electron delocalization energy (OEDE), recently proposed$^{7)}$ to estimate the degree of electron delocalization, confirms the preceding arguments. The OEDE of 1 is 1.56β whereas that of 2 is 1.33β.

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