

HOMOAROMATIC, NONHOMOAROMATIC, ANTIHOMOAROMATIC, AND DIHOMOAROMATIC CHARACTER

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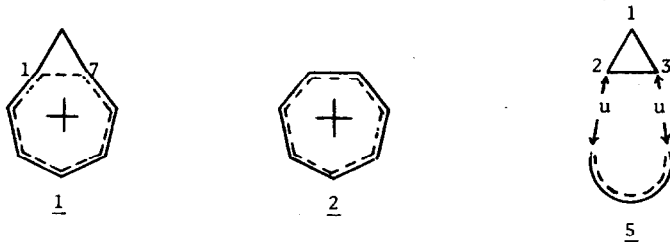
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In a separate paper<sup>1</sup> we have analysed homoaromatic character<sup>2</sup> from the standpoint of the PMO theory,<sup>3</sup> by assuming that the homoaromatic system [e.g. homotropenylium (1)] could be derived from a parent molecule [tropenylium (2)] by a reduction  $\delta\beta$  in the resonance integral of the homoconjugative linkage (1,7). Implicit in this treatment is the assumption that the cyclopropane unit is "open" and that the terminal 1,7 atoms may be treated as a perturbed part of the conjugated  $\pi$ -system.

In this communication we approach the problem of homoaromaticity by considering the interactions between an intact (closed) cyclopropane and the residual  $\pi$ -system. The conclusions remain the same, but this latter viewpoint allows a clearer insight<sup>4</sup> into the mechanism of homoconjugation.

Homoaromaticity, Nonhomoaromaticity and Antihomoaromaticity. Our starting points in this section are the Walsh<sup>5</sup> orbitals of cyclopropane<sup>+</sup> (3) and the frontier HMO orbitals of the residual  $\pi$ -electron system [exemplified in 4 by allyl (a), butadiene (b), pentadienyl (c), and hexatriene (d)]. We now consider the union<sup>3</sup> of 3 and 4 to form homoaromatic systems; clearly where the  $\pi$ -system bears a positive/negative charge, it will be appropriate to consider the cyclopropane moiety as an electron donor (from  $\psi_2$  or  $\psi_3$ )/acceptor (into  $\psi_4$ ).

1. Monocations and Monoanions. Consider first the pentadienyl cation ( $4c^+$ ), union (5) of this with 3 will lead to the homotropenylium cation (1), a known homoaromatic molecule.<sup>2</sup> As may be seen, there is a positive interaction between  $\psi_2$  and  $\chi_3$ , and we may expect electron density to flow from  $\psi_2$  into the vacant  $\chi_3$ . Where  $\chi_3$  is populated (pentadienyl anion,  $4c^-$ ), however, the cyclopropane must act as an acceptor, and the lowest vacant orbital ( $\psi_4$ ) is of the wrong

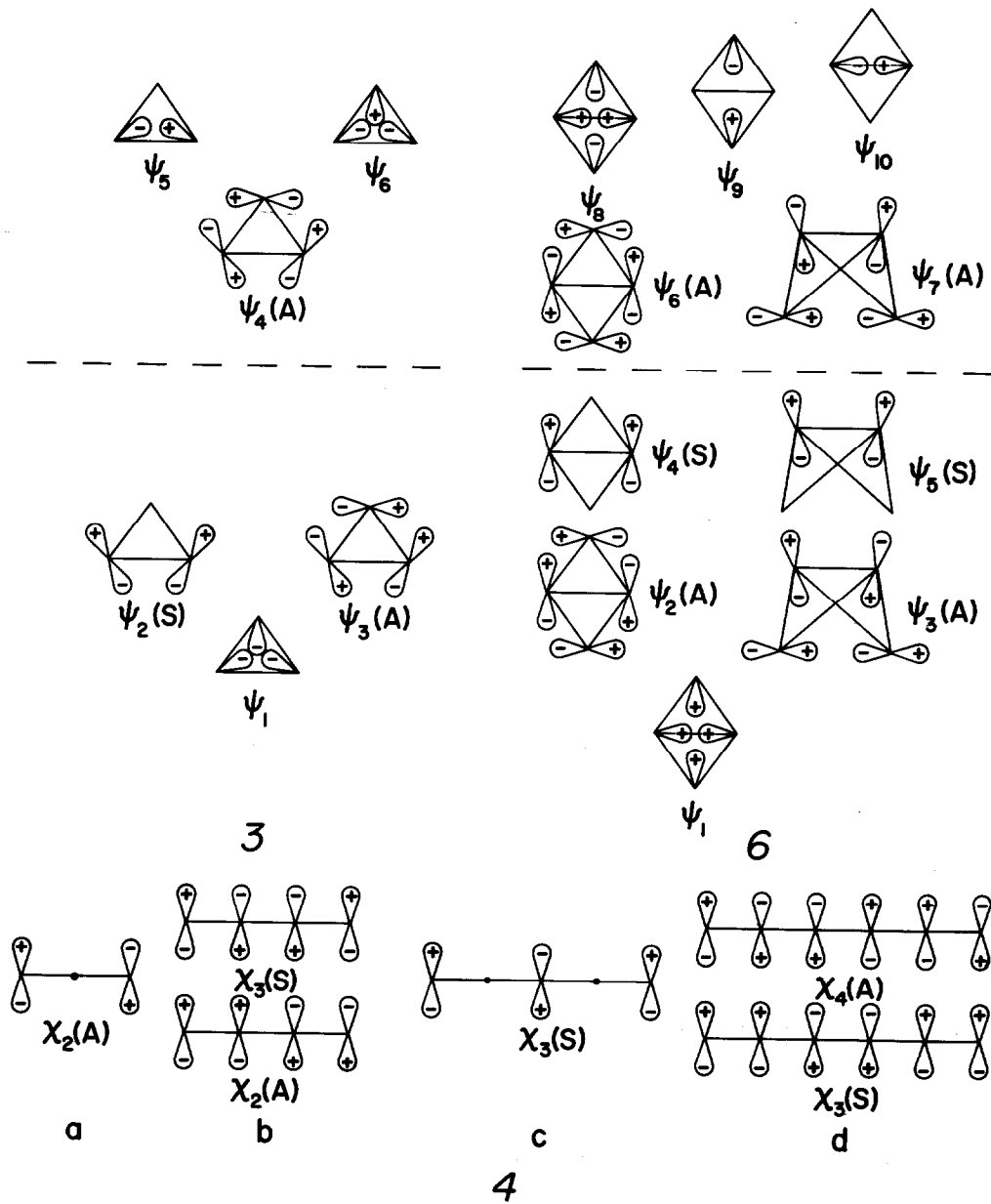


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+ A similar approach has been adopted by Hoffmann<sup>6</sup> and Gunther<sup>7</sup> in their analysis of the norcaradiene-cycloheptatriene equilibria, and by Hehre<sup>8</sup> in his reformulation of homoaromaticity in terms of Möbius<sup>9</sup> interactions

symmetry for such an interaction. Thus in this case the cyclopropane will not transmit the conjugation, and hence the homotropanyl anion is appropriately termed antihomoaromatic.<sup>2</sup>

The situation is reversed for the allyl system where the cation ( $4a^+$ ) is found to be antihomoaromatic, as the vacant orbital ( $\chi_2$ ) is of the wrong symmetry to accept electron density from  $\psi_2$ . It can however interact with  $\psi_3$ , and while this does not lead to HMO aromaticity,<sup>8</sup> it does lead to the prediction that electron density will be removed from the 1,2 and 1,3 bonds



(they become lengthened) and that considerable positive charge is transferred to C-1. This contrasts with  $4c^+$  where the interactions remove electron density from the 2,3 bond, and these differences between  $4a^+$  and  $4c^+$  seem to be borne out by theoretical<sup>10</sup> and experimental<sup>11</sup> work. The homocyclopentadienyl anion is, of course, expected to be homoaromatic (transfer of electron density from  $\chi_2$  ( $4a^-$ ) to  $\psi_4$ , but the ion has not been observed.

It is interesting to note that the homoaromatic interactions with cyclopropane involve the removal of electron density from  $\psi_2$  (cations) or the donation of electron density into  $\psi_4$  (anions); in either case this weakens the 2,3 bond and thus leads to an "open" structure for the cyclopropane unit.<sup>1,2</sup>

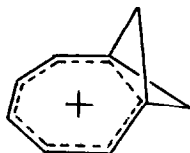
2. Dications and Dianions. Here we consider the union of the hexatriene fragment ( $4d$ ) with cyclopropane, to give homocyclooctatetraene ions. In the case of the dication ( $4d^{2+}$ ) electron density can flow from  $\psi_2$  to  $\chi_3$ , while in the case of the dianion ( $4d^{2-}$ ), the transfer is in the opposite direction, from  $\chi_4$  to  $\psi_4$ ; thus in both cases homoaromaticity is expected.<sup>2</sup>

3. Nonhomoaromaticity. It is probably not correct to say that there is no homoconjugate interaction in molecules such as the cycloheptatrienes/norcaradienes<sup>6,7,12-14</sup>, nevertheless it is appropriate to consider why the interaction seems to be weaker for neutral molecules which apparently have the potential for homoaromaticity. As noted by various authors<sup>3,15</sup> one factor which influences the interaction between a cyclopropyl unit and a neighbouring  $\pi$ -system is the relative energies of the donor-acceptor orbitals. As may be seen for the systems considered above, all the interactions have been between orbitals of one of the following combinations: bonding-nonbonding; nonbonding-antibonding; bonding-bonding; antibonding-antibonding (the first two applying to  $4a$  and  $4c$ , the other two to  $4d$ ). Where we consider union of a butadiene unit ( $4b$ ) with  $3$  to form a homobenzene, however, two interactions are possible (donation from  $\psi_2$  to  $\chi_3$  and from  $\chi_2$  to  $\psi_4$ ), and in both cases involve a bonding-antibonding pair. Evidently the energy gap between these combinations is too great and this factor, combined with the lack of a drive for charge delocalisation, reduces the interactions and the homoaromaticity of such systems. Significantly, complexation has been shown to facilitate homoconjugate overlap in neutral systems.<sup>14</sup>

Dihomoaromaticity. Finally we consider the interaction between a bicyclobutane unit and an attached  $\pi$ -system (for example  $4c^+$ ). Pomerantz and Abrahamson<sup>16</sup> constructed two alternative Walsh models (I and II in their paper) for bicyclobutane, both of which were shown to provide a good description of the chemistry of the molecule.<sup>16</sup> They differ in the hybridisation assigned to the bridgehead carbon atoms; model I assumes  $sp^2$  (olefinic) character whereas model II uses  $sp$  (acetylenic) hybridisation. The large bridgehead  $C^{13}$ -H coupling constant found in bicyclobutane derivatives indicates a 40-42%  $s$  character.<sup>16</sup> Subsequently an *ab initio* SCF calculation has been interpreted in favour of model I.<sup>17</sup> In this work we make use of model II, but irrespective of the correct model for  $6$ , it is clear that appropriate substitution at the bridgehead may somewhat alter the preferred mode of hybridisation. The analysis given by Pomerantz and Abrahamson (model II)<sup>16</sup> is reproduced in diagrammatic form above (6).

Most of the degeneracy would be lifted in a more sophisticated calculation,<sup>17</sup> but the main features, for our purposes, will remain, *viz.* the occurrence of  $\psi_4$ , as a high lying occupied orbital. Obviously this orbital is of just the type we used above for donation

into  $\chi_3$  of  $4c^+$  to give the homotropenylium cation (1). It will be of great interest to see whether such an interaction can occur for 6 and whether or not the dihomotropenylium\* cation (7) is to remain a theoretical curiosity.



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\* This appears to be the only suitable prefix remaining in the lexicon.<sup>2</sup>

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