Tetrahedron Vol. 44, No 24, pp. 7611 to 7620, 1988
Printed in Great Britain

0040-4020/88 $3.00 + .00

Rehybridization and the Chemical Reaction: POAV and 3D-HMO Analysis

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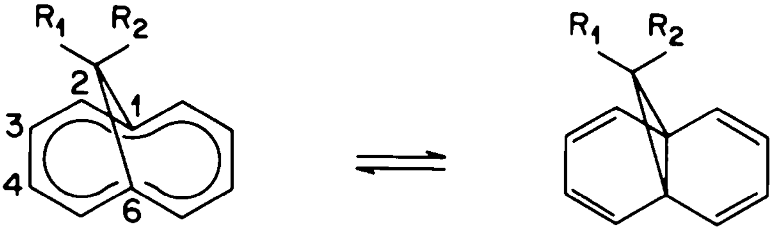
(*Received in USA* 28 *April* 1988)

Abstract: In this study chemical reactions are examined from a new standpoint — *rehybridization*. With the possible exception of oxidation-reduction processes, all chemical reactions involve rehybridization. Bond-making and bond-breaking processes are nothing more than changes in hybridization. In the present study two catogories of pericyclic reactions are examined with the π-orbital axis vector (POAV) analysis and the three-dimensional (3D) HMO theory. The first makes use of a series of related molecular structures derived from X-ray crystallography which provide information on the reaction pathway between the valence tautomers 1,6-methano[10]annulene (**1a**) and the bisnorcaradiene (**1b**). The second category involves structures calculated by Dewar and coworkers along the minimum energy reaction pathway of the Cope rearrangement of 1,5-hexadiene (**2**). The analysis provides a clear delineation of the structural and electronic changes which accompany chemical reaction. The *sense* of the π-orbital axis vectors at the bridgehead atoms is shown to be the determining feature in dividing the potential surface of **1** between bridged-[10]annulene (**1a**) and bisnorcaradiene (**1b**).

In this work I wish to examine chemical reactions from a new standpoint — *rehybridization*. With the possible exception of oxidation-reduction processes, all chemical reactions involve rehybridization. In the present article we shall focus on pericyclic reactions, but it is important to bear in mind that changes in hybridization are central to most chemical reactions. Bond-making and bond-breaking processes are nothing more than changes in hybridization.

The rehybridization which takes place in molecules along the reaction pathway will be followed with the π-orbital axis vector (POAV)$^{1-3}$ analysis and the three-dimensional Huckel molecular orbital (3D-HMO)^{4} theory. The POAV approach provides a basis for the separation of σ and π orbitals which is valid in all (1-3)-dimensions.^{5} A π-orbital is defined to be that hybrid orbital which is locally orthogonal to the σ-orbitals.^{5} The resulting π-orbitals are treated with the 3D-HMO theory to produce reduced resonance integrals, which are comparable with the quantities (β) which occur in the standard HMO theory for planar π-electron systems. The approach has been fully documented in previous publications where the analysis was applied to the (static) structures of nonplanar conjugated organic molecules.$^{1-6}$ The new feature in the present study is the dynamical aspect of the molecular structures and the involvement of transition states.

Dedicated to Michael Dewar in appreciation of his seventieth year as a maverick.



1a **1b**

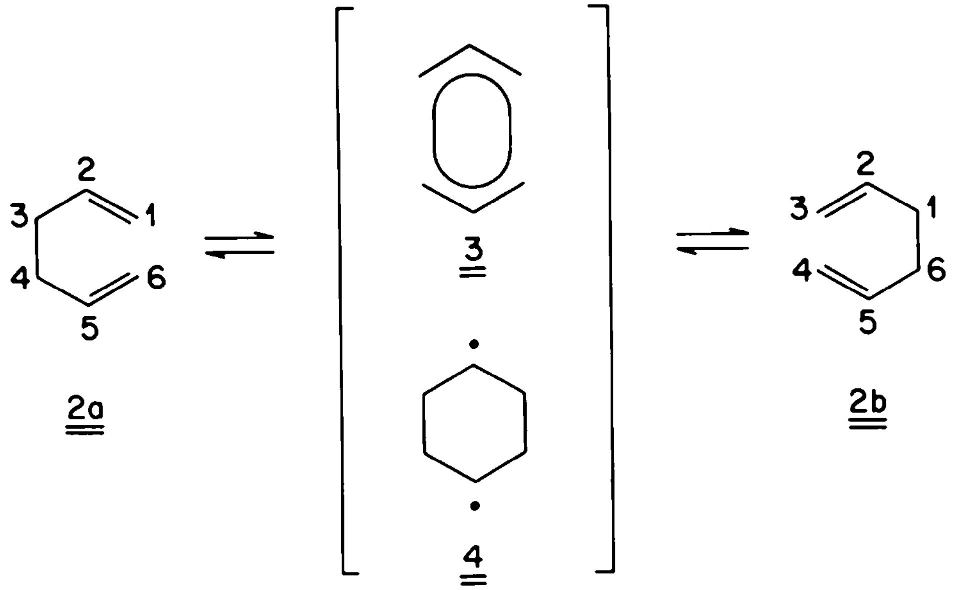
The reactions for study in the present work fall into two categories. The first makes use of a procedure initially introduced by Bürgi and Dunitz[7–8] which relies on a series of related molecular structures derived from X-ray crystallographic analyses. In certain cases it has been shown that the structures correlate with points along a reaction coordinate.[7,8] A particularly well documented[9–12] example is the pericyclic reaction involving the valence tautomers **1a** and **1b** which entails the formal conversion of C-1 and C-6 between sp^2 and sp^3 hybridization.

The equilibrium between bridged-[10]annulene (**1a**) and bisnorcaradiene (**1b**), is extremely delicate and as a result it has been possible to experimentally characterize compounds corresponding to each structural extreme: **1a**, $R_{1,6} = 2.269$ Å ($R_1 = R_2 = F$)[13] and **1b**, $R_{1,6} = 1.539$ Å ($R_1 = R_2 = CN$).[14] Perhaps even more surprising is the discovery that certain derivatives crystallize with a 1,6 bond of intermediate length,[15–19] and in a certain sense these structures therefore provide a snapshot of the minimum energy reaction pathway between **1a** and **1b**.[12,15] In the case of $R_1 = Me$, $R_2 = CN$, for example, structures have been obtained with $R_{1,6} = 1.623$, 1.712, 1.782 and 1.851 Å.[16,17] The potential surface in these compounds is extremely flat to the point that this single molecule can crystallize with four quite different structures depending on crystal phase, temperature and location in the unit cell.[15–17]

In the second category is a study of the Cope rearrangement in which we make use of theoretically derived structures which have been obtained at various points along the minimum energy reaction pathway (MERP); the structures have been fully optimized with respect to all geometrical parameters with the exception of a convenient reaction coordinate.[20–22] Although it is well known that reacting molecules are unlikely to actually follow such a pathway to the reaction products, this type of analysis is heuristically useful and is wide spread in chemistry. In the Cope rearrangement of 1,5-hexadiene (**2**), C-1 and C-6 rehybridize from sp^2 to sp^3, whereas C-3 and C-4 undergo the reverse transformation.

The mechanism of the Cope rearrangement of **2** remains the subject of discussion in the literature,[20–24] and there are two mechanistic extremes which may be envisaged for this reaction.

The first involves an aromatic transition state (**3**)[23] of the type originally envisaged for pericyclic reactions by Woodward and Hoffmann,[25] whereas a second possibility incorporating a biradicaloid transition state (**4**) of the type suggested by Doering and coworkers[26] has been advanced by Dewar and coworkers.[20,21,24] We have been supplied with the structures of both transition states and a full reaction pathway for the biradicaloid process as calculated by the AM1 procedure.[20,21,24] Although there remains some dispute concerning the relative energies of these two reaction pathways, there is remarkable agreement regarding the structures of the transition states (or intermediates) involved in the rearrangement.



Calculational

The equations required to effect the POAV and 3D-HMO analyses have been incorporated into a FORTRAN computer program entitled POAV3, which has been deposited with the Quantum Chemistry Program Exchange.[27] The atomic coordinates of the molecule or molecular fragment of interest, are the only data which are required for the execution of the POAV3 program.[1-6]

The geometries for 1: $R_1 = R_2 = CN$, at −123°C ($R_{1,6} = 1.539$ Å);[14] $R_1 = Me$, $R_2 = CN$, β phase at −100°C ($R_{1,6} = 1.623$ Å);[17] $R_1 = Me$, $R_2 = CN$, β phase ($R_{1,6} = 1.712$ Å);[17] $R_1 = R_2 = Me$ ($R_{1,6} = 1.770$ Å);[19] $R_1 = Me$, $R_2 = CN$, α phase ($R_{1,6} = 1.782$ Å);[16] $R_1 = R_2 = Me$ ($R_{1,6} = 1.826$ Å);[19] $R_1 = Me$, $R_2 = CN$, α phase ($R_{1,6} = 1.850$ Å);[16] $R_1 = R_2 = H$, at −128°C ($R_{1,6} = 2.235$ Å);[18] $R_1 = R_2 = F$, at −100°C ($R_{1,6} = 2.269$ Å),[13] were obtained by an appropriate transformation of the unit cell coordinates published by Simonetta and coworkers.[13-19] The parameters calculated in the POAV/3D-HMO analysis were averaged within C_{2v} symmetry.

The geometries along the reaction coordinate of the Cope rearrangement were supplied by E. F. Healy and C. Jie from AM1 calculations carried out by Dewar and coworkers.[20-22] A complete reaction pathway was made available for the chair biradical mechanism, which was found to be the preferred route in the AM1 studies. For comparison purposes the boat aromatic transition state was also included.

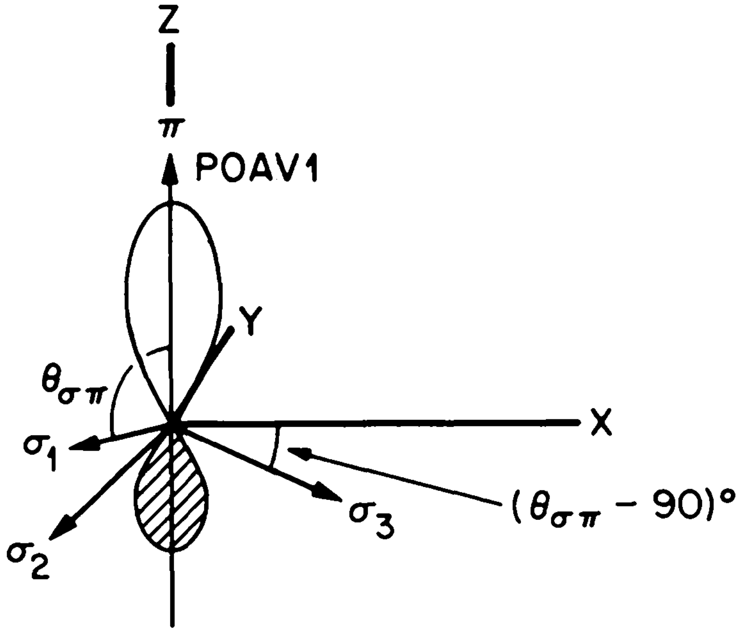


Figure 1. Definition of $\theta_{\sigma\pi}$ [angle made by the π-orbital to each of the σ-bonds], $(\theta_{\sigma\pi} - 90)°$ [pyramidalization angle], and the sense of the π-orbital axis vector [POAV1]. In this construct the local (X,Y) plane is taken to be perpendicular to the POAV1.

Results and Discussion

Potential Surface for the 1,6-Bridged[10]annulene (**1a**) *and Bisnorcaradiene* (**1b**) *Reaction.* The one-center POAV analysis is presented in the form of the pyramidalization angle $(\theta_{\sigma\pi}-90)°$ ($\theta_{\sigma\pi}$ is the common angle made by the σ orbitals to the π orbital, POAV1) and the s character m in the π orbital (s^mp, obtained by the imposition of orbital orthogonality, POAV2).[1-4] The sense of the π-orbital axis vector[3,4] is defined in Figure 1.

It may be seen from Figure 2 (and 3) that the potential surface of **1** is divided into two parts according to the sense of the π-orbital axis vectors at C−1 and C−6 which is shown in the lower part of the Figures. For $R_{1,6} < 1.9$ Å the π-orbital axis vectors at these carbon atoms point downward (taking the direction of the bridge group to be upward), whereas for $R_{1,6} > 2.2$ Å the 1,6 carbon atoms pyramidalize upward. It should be noted that the remaining perimeter atoms are *always* pyramidalized so that the π-orbital axis vectors point upward. It is clear therefore that the sense of the π-orbital axis vectors at C−1 and C−6 is intimately connected with the electronic and molecular structure of derivatives of **1**. The small energetic expense which accompanies modest degrees of pyramidalization[5] probably explains the absence of structures with $1.9 \text{ Å} > R_{1,6} > 2.2$ Å.

The two-center POAV2/3D-HMO analysis for 1 is presented in Figure 3, in the form of the ρ values which provide reduced resonance integrals $\rho\beta$ which are suitable for use in an HMO calculation.[4–6] In the present work ρ^B values are employed; these quantities are obtained by scaling the calculated overlap integral between POAV hybrid orbitals with the nearest-neighbor p_π, p_π overlap integral for benzene.[4]

The analysis throws further light on the point raised previously with respect to the direction of pyramidalization of C−1 and C−6. It may be seen that for $R_{1,6} > 2.2$ Å where the pyramidalization of these atoms is upward which is in the same direction as the other conjugated atoms, the overlap around the perimeter is very high, with ρ^B values of all of the bonds close to unity. The 2,3 and 3,4 bonds maintain good overlap throughout the whole potential surface with $\rho^B \sim 1.0$ and in the region 1.7 Å $< R_{1,6} <$ 1.9 Å the 1,6 (homoconjugate) bond also maintains a ρ^B value close to unity, and this behavior is reminiscent of the homoconjugate bond in the homotropenylium cation.[6] Given this situation it is appropriate to enquire as to whether this region of the potential surface, represents a fully developed homonaphthalene structure. That this situation does *not* hold may be attributed to the poor overlap achieved by the 1,2 bonds. The largest $\rho^B_{1,2}$ value is 0.706 which occurs at $R_{1,6} = 1.851$ Å, which is probably sufficient to inhibit delocalization and aromatic character in the molecule, as this bond type occurs four times in the perimeter. In a related sterically crowded 1,6-methano[10]annulene it was found that two bridgehead bonds with $\rho^B = 0.437$ was sufficient to inhibit delocalization.[4] The experimental evidence also suggests that the molecules falling in this region of the potential surface are not fully delocalized and should be regarded as essentially nonaromatic.[9–11]

The low $\rho^B_{1,2}$ values seem to be directly attributable to the direction of pyramidalization of C−1 and C−6. We have previously noted that the POAVs tend to have the same sense,[4] and this is maintained in the ideal homoaromatic molecule, homotropenylium cation[5,6] for 1.6 Å $< R_{1,7} <$ 2.6 Å, where C−1, C−2, C−6 and C−7 are always pyramidalized in the opposite direction to the bridge group. The reason homotropenylium cation is homoaromatic, and 1 is nonhomoaromatic for 1.7 Å $< R_{\text{homo}} <$ 2.0 Å, may therefore be attributed to the sense of pyramidalization at the homoconjugate atoms and their nearest neighbors. The additional conformational restraints present in the bicyclic 1 may dictate to some extent the preferred sense of pyramidalization.

For $R_{1,6} <$ 1.7 Å, the homoconjugate bond (1,6) becomes the strongest π-bond in the molecule; the same behavior was noted for the homotropenylium cation.[6] Simonetta and coworkers[15] have carried out a charge density topological analysis of the tautomerism of 1 at the HF/STO-3G theoretical level. On this basis they conclude that the 1,6 bond in 1 vanishes between $R_{1,6} = 1.770$ and 1.782Å for which we find $\rho^B = 1.085$ and 1.099.

Potential Surface for the Cope Rearrangement of 1,5-Hexadiene (2). The one-center analysis of the Cope rearrangement of 1,5-hexadiene(2) is shown in Figure 4, and it may be seen that the π-hybridizations span the full range: $(\theta_{\sigma\pi}-90)° = 0 - 19.7°$ (POAV1; note that 0° is planar and 19.7° is tetrahedral geometry),[5] and $m = 0 - 1/3$ (s^mp, POAV2; note that $s^0p \equiv p$ and $s^{1/3}p \equiv sp^3$).[5] It is interesting to note that C−2 exhibits a high degree of planarization in reaction and product, but becomes quite pyramidalized near the transition state (TS). As the curve represents the biradicaloid pathway it is not surprising to find a high degree of rehybridization at the TS (4) ($\Delta R \sim 0$), as the 1,6 and 3,4 bonds are essentially fully formed σ-bonds. The open points correspond to the aromatic boat TS (3) and here the rehybridization is much less − comparable to that found for 1 and homotropenylium cation.[6]

In fact the hybridizations found in 3 and 4 (Figure 4) are remarkably close to the prescription provided by Doering and coworkers:[26] "The geometry to be assigned to this "concerted" transition state has remained undecided between the familiar four-centered π-complex, in which the 3,4-bond can be described as having been transformed from sp^3−sp^3 to half p − half p and the 1,6 no-bond has become half p − half p, and the cyclohexane-2,5-diyl diradical in which the 3,4-bond is essentially unchanged and the 1,6-bond is now an equally fully formed sp^3−sp^3 bond". As may be seen from Figure 4, the hybridizations of C-1, 3,4 and 6 at the aromatic (π-complex) transition state (3) are approximately $s^{0.063}p$ (POAV2) with $\theta_{\sigma\pi} = 9.8°$ (PAOV1). The asymmetrical biradical TS(4, $R_{1-6} = 1.682$Å, $R_{3-4} = 1.622$Å)[20–22] has hybridizations at C-1,3 of $s^{0.157}p$ (POAV2) with $\theta_{\sigma\pi} = 14.7°$ (PAOV1) and at C-3,4 of $s^{0.202}p$ (PAOV2) with $\theta_{\sigma\pi} = 16.2°$ (POAV1), whereas the symmetrical biradical intermediate (4, $R_{1-6} = R_{3-4} = 1.654$Å)[20–22] has hybridization at C-1, 3,4 and 6 of $s^{0.187}p$ (POAV2) with $\theta_{\sigma\pi} = 15.7°$ (POAV1).

The two-center analysis is given in Figure 5, and again it may be seen that the 1-6 and 3-4 bonds near the biradicaloid TS have ρ^B values much stronger than a normal π-bond and are better thought of as σ-bonds (4). The 1-2 and 2-3 bonds appear as well-developed π-bonds. The aromatic boat TS (3, open points) has ρ^B values reasonably close to unity and it is clear that this structure has an orbital topology remarkably close to that of benzene. This is quite consistent with the interpretation of pericyclic reactions by Woodward and Hoffmann,[25] Evans,[28] Dewar[29] and Zimmerman.[30]

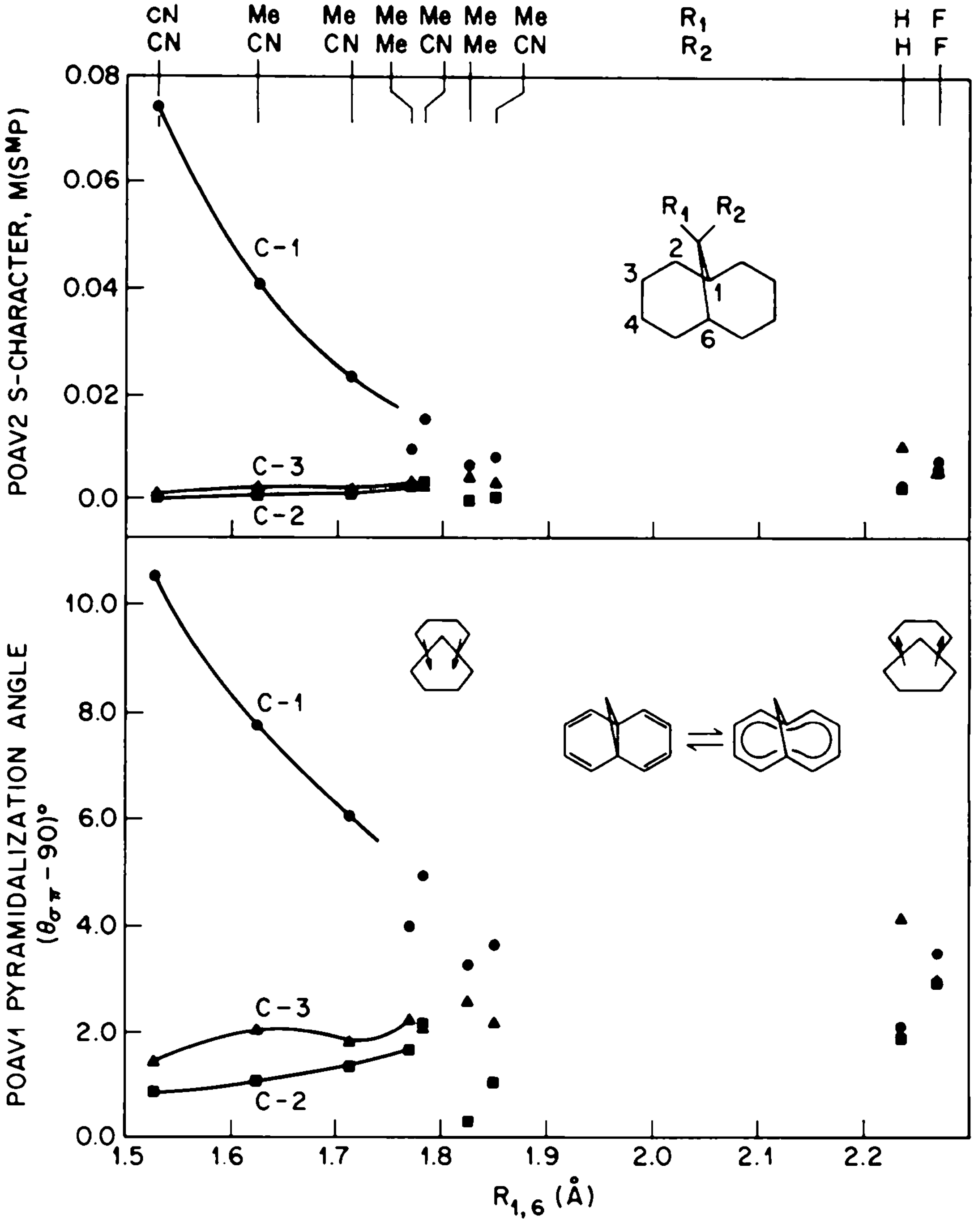


Figure 2. One-center POAV analysis of the structures of 1 (see Figure 1).

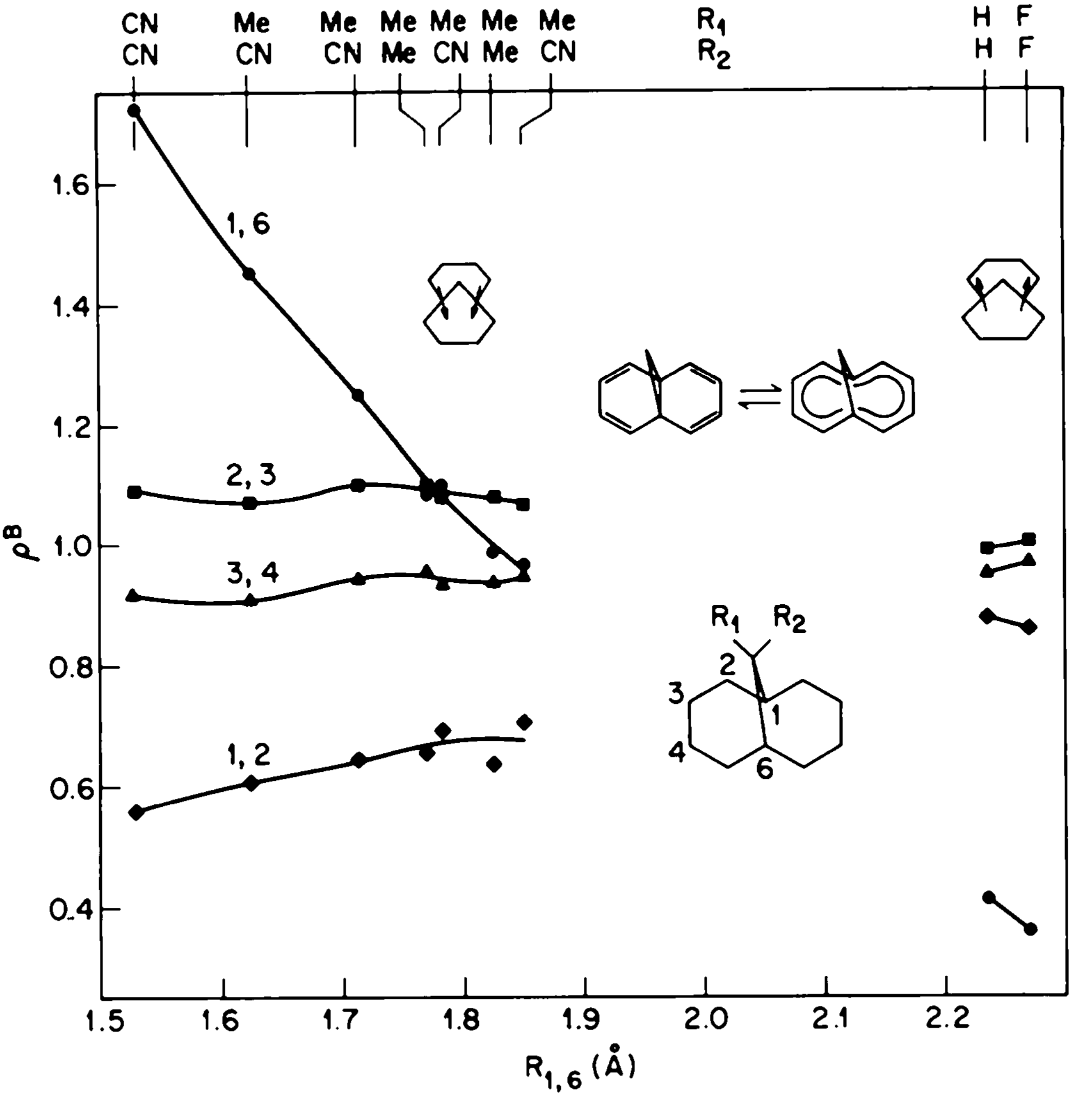


Figure 3. Two-center POAV2/3D-HMO analysis of the structures of **1**, where ρ^B is the reduced resonance integral (units of β) for the conjugated bonds.

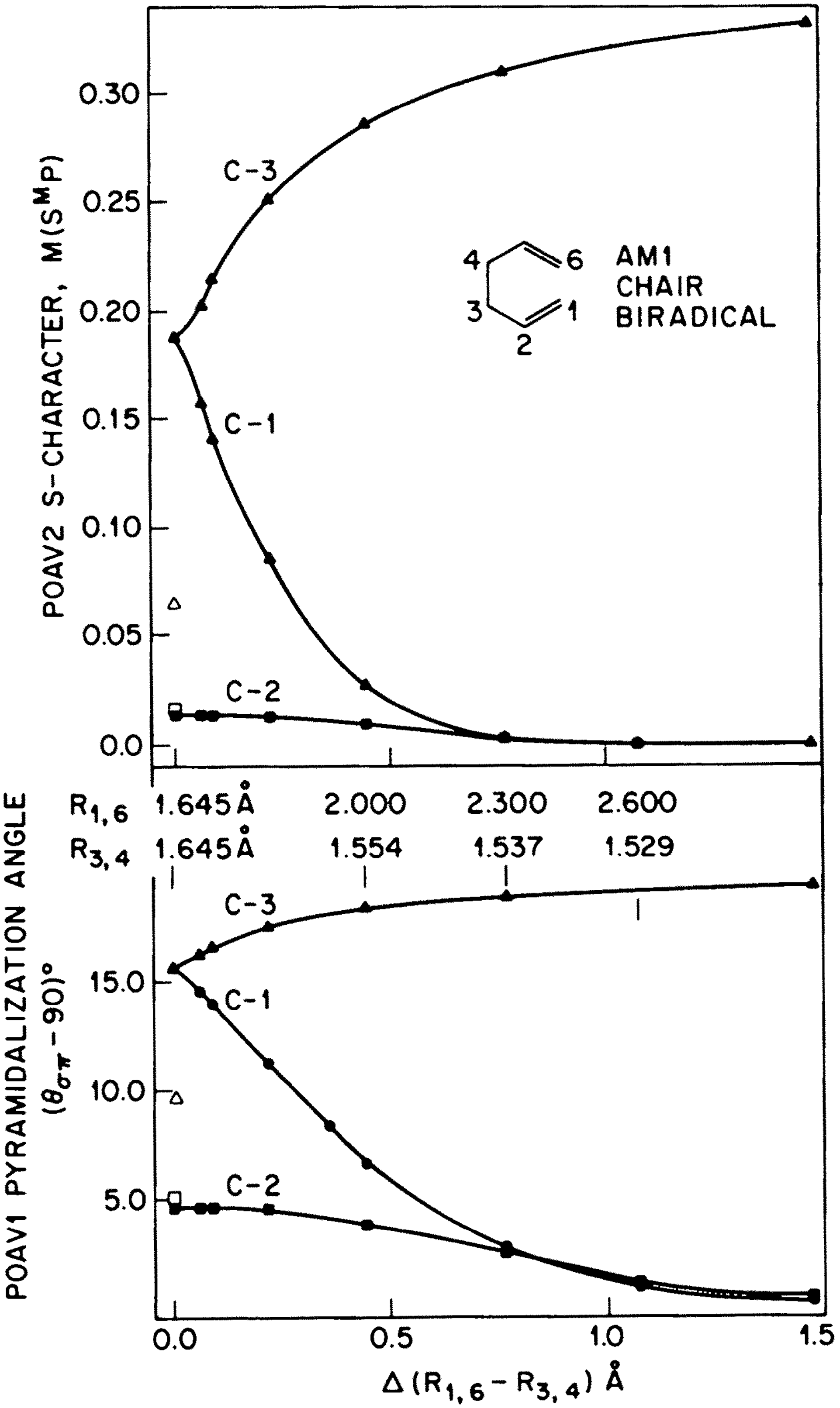


Figure 4. One-center POAV analysis of the potential surface of 2 (see Figure 1). The solid points are for the chair biradical pathway (via 4), and the open points correspond to the boat aromatic TS (3).

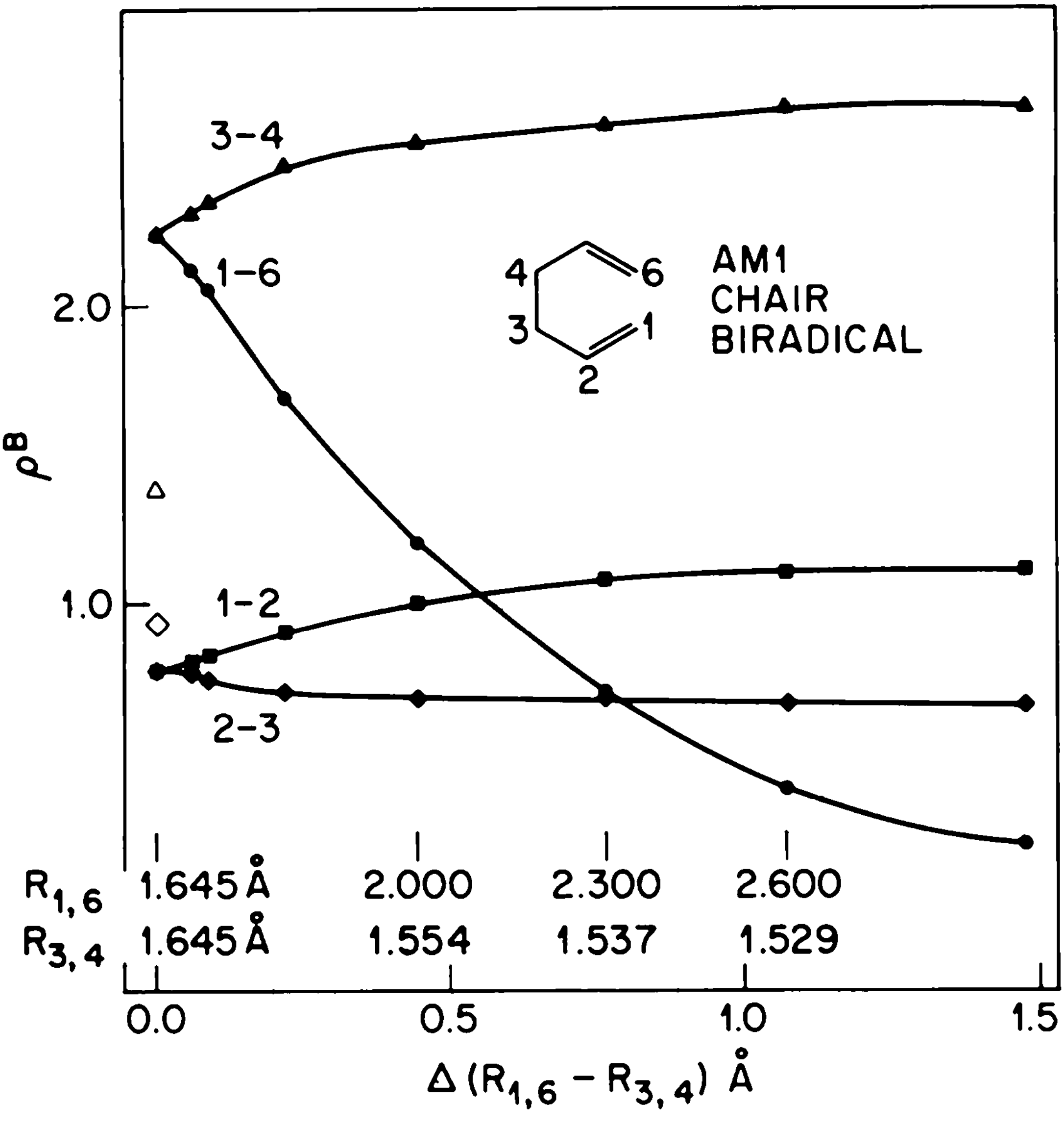


Figure 5. Two-center POAV2/3D-HMO analysis of the potential surface of 2, where ρ^B is the reduced resonance integral (units of β) for the conjugated bonds. The solid points are for the chair biradical pathway (via 4), and the open points correspond to the boat aromatic TS (3).

Acknowledgement

It is a pleasure to acknowledge discussions with L. T. Scott regarding the pyramidalization in bridged-annulenes. I am also grateful to E. F. Healy, C. Jie and M. J. S. Dewar for making available the AM1 geometries for the Cope rearrangement of 1,5-hexadiene.

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