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On the Barriers to Thermally Allowed Reactions and the Elusiveness of Neutral Homoaromaticity

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Abstract: As a model for the phenomena described in the title, and, more specifically, to elucidate the factors preventing rapid interconversion of 1,5,9-cyclododecatriyne with triscyclobutenabenzene, the thermally allowed D_{3h}-symmetrical cyclotrimerization of acetylene to benzene has been studied by MINDO/3 and ab initio STO-3G methods. In spite of the symmetry-allowed nature of the reaction, appreciable distortion of the acetylenes must occur before substantial frontier orbital interactions can switch electron density from bonding regions in the reactant to bonding regions in the product. Stabilizing HOMO-LUMO interactions between π systems only ensue when the isolated molecules have been substantially distorted. Overlap of nonconjugated π systems increases the interactions between filled orbitals, but this destabilizes—not stabilizes—the molecules. In a sense, the systems designed to produce neutral homoaromatic stabilization are somewhat "antiaromatic" instead. Aromatic or homoaromatic interactions occur because of stabilizing π interactions, but only at the expense of the energy required to distort the σ framework. In cyclic conjugated systems, the σ framework is shown to be relatively insensitive to geometrical distortions so that π delocalization can afford aromaticity in $4n + 2$ π electronic systems.

Introduction

The energetic advantage of aromatic cyclic delocalization is a cornerstone of organic chemistry. Nevertheless, thermally allowed reactions which are very exothermic may have substantial activation barriers, in spite of the fact that such reactions involve aromatic transition states. Furthermore, neutral molecules designed to provide maximum overlap between a homoconjugated cyclic array of $4n + 2$ electrons do not show any of the homoaromatic stabilization expected for such systems.[2a]

In order to probe the source of the resistance to aromaticity common to both of these examples, we have performed model calculations on the trimerization of acetylene, a prototypical thermally allowed cycloaddition which can also serve as a model for potentially homoaromatic uncharged molecules. The transition state of a thermally allowed reaction is that point where stabilizing ("charge transfer") HOMO-LUMO interactions overcome the energy of distortion of, and the closed-shell repulsion between, the component π systems. Our results indicate that inducement of stabilizing interactions between filled and vacant orbitals of interacting π systems requires appreciable distortion of the constituent π subunits in order to occur. This conclusion implies that overlap between undistorted π systems will be destabilizing. We contrast this to authentic aromatic systems.

Activation Barriers to Exothermic Thermally Allowed Reactions

Even though the trimerization of acetylene to form benzene is extremely exothermic ($\Delta H° = -143$ kcal/mol), the reaction takes place only to a small extent at temperatures in excess of 400 °C, and many other hydrocarbons are formed in large amounts.[2b] Recently, Vollhardt and co-workers synthesized 1,5,9-cyclododecatriyne,[3] a molecule which would appear likely to cyclize readily, since it has the three acetylene units held more or less rigidly; thus, entropy factors[4] should not prohibit reaction. Nevertheless, this molecule undergoes thermal rearrangements only above 200 °C to form products apparently arising from triscyclobutenabenzene.[3] The latter hydrocarbon has now been synthesized[5] by Thummel et al.[5] and is quite stable thermally. We have also carried out calculations on this interconversion, and find a high barrier similar to that of the parent trimerization.[6] Thus, there is substantial impedance to the Woodward-Hoffmann thermally allowed trimerization of acetylene. Assuming that the A factor of a termolecular reaction is 10^2 less than that of a bimolecular,[4] the concerted trimerization of acetylene must have an $E_{\text{act}} >$ 36 kcal/mol in order to not be observed at 620 K.

What is the origin of the apparently high barrier to interconversion of three acetylenes and benzene? The question is actually more general: why do highly exothermic, thermally allowed pericyclic reactions have barriers at all, even though the reactant and product orbitals smoothly transform into each other? This question is of fundamental significance to our understanding of the considerable success of frontier molecular orbital treatments of reactivity. That is, although reactivity frequently can be predicted from considerations of stabilizing interactions between filled and vacant orbitals of reactants,[7] such treatments predict no activation barriers at all.[8]

Salem and co-workers recently showed that, in the Diels-Alder reaction of butadiene with ethylene, the HOMOs of both

Table I. Energies and Geometries of Various Points on the Computed D_{3h} Reaction Path for Acetylene Trimerization[a]

point	rel energy	$r(C_1C_6)$	$r(C_1C_2)$	$r(CH)$	∠HCC
1	0 ($\Delta H_f° = 173.2$)	∞	1.196	1.071	180
	(0) ($E = -227.5688$ au)	∞	(1.168)	(1.065)	(180)
1A	0.1	16.72	1.196	1.071	180.0
2	0.8	4.60	1.195	1.071	179.9
3	4.2	3.73	1.195	1.071	179.4
4	23.8	2.87	1.194	1.071	175.8
5	33.3	2.69	1.194	1.071	173.7
6	45.7	2.52	1.196	1.071	170.6
7	60.2	2.35	1.200	1.072	166.4
	(64.0)	(2.34)	(1.170)	(1.08)	
8	72.7	2.16	1.213	1.075	159.7
	(71.0)	(2.16)	(1.198)		
9	26.1	1.92	1.353	1.093	129.7
	(−15.6)	(1.92)	(1.347)		
10	−55.0	1.74	1.373	1.096	126.0
11	−121.6	1.56	1.389	1.100	122.9
12	−144.8	1.407	1.407	1.105	120.0
	(−202.9)	(1.397)	(1.397)	(1.084)	(120.0)
13	−143.2	1.375	1.406	1.107	119.4

[a] Values are from MINDO/3 calculations except for values in parentheses, which are from STO-3G calculations. Distances are in ångstroms, angles in degrees.

molecules increase and the LUMOs decrease in energy during the early stages of the reaction.[9] Their work apparently contradicts the frontier orbital treatment, which suggests that these orbitals will mix, with the filled orbitals being stabilized and the vacant destabilized, in early stages of the reaction.

In order to probe these effects in a model system, we have carried out calculations on the thermal trimerization of acetylene, described in the following section.

Acetylene Trimerization

Both MINDO/3[10] and ab initio (STO-3G basis)[11] calculations were carried out for the trimerization of acetylene. D_{3h} symmetry was enforced, but aside from this restraint all angles and lengths were fully optimized. Each calculation was performed by fixing the distance from the center of each acetylene to the center of mass of the C_6H_6 system. The results of these calculations are given in Table I and Figure 1, where the heavy line is drawn through the MINDO/3 energies. The maximum in this curve is not necessarily the transition state for this reaction since the surface was not explored thoroughly. Furthermore, McIver has proposed that transition states of lesser symmetry would be expected for such reactions.[12]

The experimental heat of reaction (−143 kcal/mol) is reproduced admirably by the MINDO/3 calculations, which give a heat of reaction of −145 kcal/mol. In spite of this enormous exothermicity, the reaction is calculated to have a $\Delta H^{\ddagger}$ of about 80 kcal/mol for the D_{3h} pathway.

Ab initio calculations using the STO-3G basis set[11] were carried out for a few points, connected by the dashed line in Figure 1. The same constraints were kept as for the MINDO/3 calculations, except that the CH distances were also fixed at 1.08 Å. Although the calculated energy of reaction (−207 kcal/mol) is far too negative (compare −152 kcal/mol using heats of formation corrected for zero-point energies[13]), the calculated activation energy is remarkably similar to that found by MINDO/3. Furthermore, the various geometrical parameters calculated by the two methods differ in a similar fashion along the reaction pathway (Table I).[14] Configuration interaction would undoubtedly lower the calculated activation energy appreciably, but the main point here is not to predict the precise activation energy for this reaction, but to investigate the origin of the relatively high barrier.

Before the transition state is reached, the C_6H_6 ensemble resembles three distorted acetylenes, whereas after the transition state the system is clearly a distorted benzene. The bonding changes occur rather suddenly at the transition state. Further insight can be obtained by inspecting the behavior of the high-lying filled and low-lying vacant orbitals along the chosen reaction path. As the molecules approach one another, there is a smooth evolution of the three occupied and three vacant π MOs of three acetylenes into those of benzene. However, the orbitals which are initially π orbitals in the isolated acetylenes, but lie in the plane of the three acetylenes for this reaction path, exhibit behavior like that observed earlier for the Diels-Alder reaction by Townshend et al.[9] That is, the in-plane occupied π MOs increase in energy until the transition state, whereupon they are suddenly stabilized; the vacant LUMOs exhibit the opposite behavior. According to MINDO/3, the in-plane acetylene π orbitals are destabilized from −10.8 eV in acetylene to −8.6 eV in the transition state, and then are stabilized to −10.4 eV in benzene. The corresponding LUMO's drop from +2.2 eV in acetylene to +0.8 eV in the transition state, and then rise to +3.0 eV in benzene.

The reason for this behavior, which apparently contradicts the expectations based on frontier molecular orbital theory, can be discerned upon inspection of the relevant orbitals of three weakly interacting acetylenes and of benzene (Figure 2). The acetylene in-plane π orbitals and the symmetry-adapted combinations of the three "new" σ bonds of benzene are shown in this figure to emphasize the bonding changes which occur in this reaction. In the benzene molecule, these three σ orbitals are mixed extensively with other π orbitals. Inspection of these orbitals suggests the origin of the high barrier to reaction. The electron density localized in the bonding regions between the atom pairs 1-2, 3-4, and 5-6 in the reactants must be transferred to different bonding regions (2-3, 4-5, and 6-1) in the product, and this bond switching is resisted until the transition state is reached. For example, in MINDO/3, the bond order of each newly forming σ bond changes from 0.1 before the transition state (point 8) to 0.9 just after the transition state (point 9). At the same time the bond order of each acetylene in-plane π orbital changes from 0.9 to 0.3.

This is hardly a unique situation: in all thermally allowed pericyclic reactions, indeed in all chemical reactions, electron density must be transferred out of bonding regions in the reactants into bonding regions in the product. The interesting point exemplified dramatically in the acetylene trimerization is that this transfer of electron density does not occur to any appreciable extent until the reactants have been sufficiently distorted away from stable closed-shell geometries.

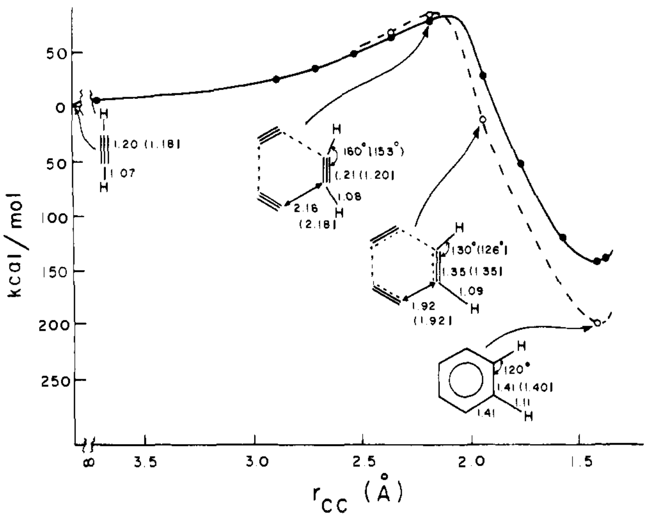
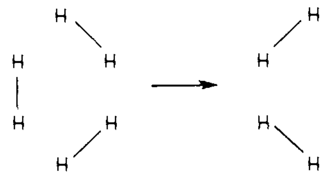


Figure 1. MINDO/3 (●, —) and ab initio STO-3G (○, ---) D_{3h} surfaces for acetylene trimerization.

A reaction which is topologically equivalent to, but conceptually much simpler than, the acetylene trimerization is the hexagonal bond-switching process of hydrogen. This reaction has been studied computationally by Wright,[15] by Dixon, Stevens, and Herschbach,[16] and by Thompson and Suzukawa.[17] For this simple reaction, an activation energy of 66 kcal/mol is predicted for the D_{6h} transition state, considerably below the hydrogen bond dissociation energy of 109.5 kcal/mol, but remarkably high for a thermally allowed reaction. Shock-tube experiments indicate a barrier of 42 kcal/mol for the reaction of H_2 with D_2.[15] Figure 3 shows a correlation diagram for the $3H_2$ reaction. On the far left and far right of this diagram, the orbitals of three weakly interacting hydrogen molecules are shown. An orbital symmetry correlation diagram for this reaction would connect horizontally the reactant and product orbitals, but such a correlation diagram does not reveal the origin of the activation barrier.



It is instructive to construct this correlation diagram in a stepwise fashion. For example, in the middle of the diagram, two of the orbitals are shown which would be formed if the nuclear motions occurred without change in the reactant orbitals. Such an artificial process implies that an orbital crossing occurs, since the degenerate HOMOs of the reactants become antibonding as the nuclear motions occur. However, such a crossing never materializes, since the degenerate HOMOs and degenerate LUMOs are of the same symmetry and mix. The bonding orbitals of the reactants then smoothly correlate with the bonding orbitals of the product. However, since the HOMO–LUMO mixing is inversely proportional to the difference in energy between these orbitals, no substantial mixing will occur until the H_2 bonds are appreciably stretched. The other HOMO and LUMO of the degenerate sets behave similarly. The behavior resembles somewhat that of a thermally forbidden reaction, but for an orbital symmetry allowed reaction the intended HOMO–LUMO crossing is avoided at the orbital interaction (one-electron) level, while for a thermally forbidden reaction the crossing is avoided only at the configuration interaction (two-electron) level. In order to reach a geometry where extensive charge-transfer interactions occur, considerable energy must be input to distort the hydrogen molecules and to overcome the repulsion resulting from overlap of the filled orbitals of the hydrogen molecules.

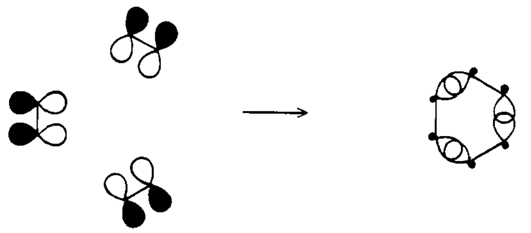


Figure 2. In-plane π orbitals of three acetylenes and three localized σ orbitals of benzene.

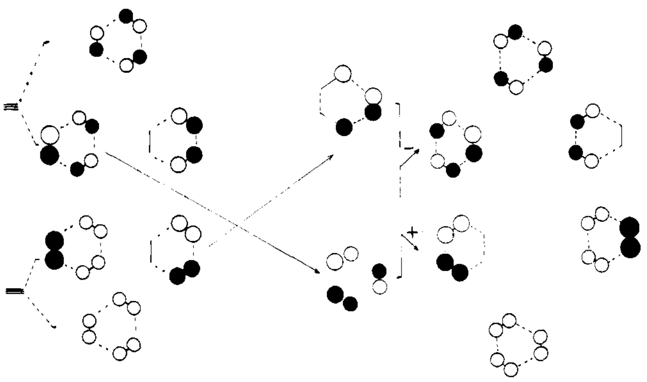


Figure 3. Stepwise correlation diagram for the bond-switching reaction of three hydrogen molecules.

Returning to the early stages of the acetylene trimerization, there is net destabilization upon interaction of three acetylenes, because the large HOMO–LUMO gap prevents appreciable charge-transfer interaction, and the overlap of filled orbitals gives net destabilization. The acetylenes must distort substantially before the HOMO–LUMO gap decreases enough for stabilizing interactions to overcome destabilizing ones. Once the charge-transfer or delocalization (HOMO–LUMO) interaction has become sufficient to transfer appreciable electron density into product bonding regions, further distortions are stabilizing and lead to the equilibrium geometry of benzene. Calculations on the distorted acetylenes by STO-3G indicate that 60 kcal/mol of the 80 kcal/mol barrier is due to the energy required to distort the three acetylenes to the "transition state" geometries. The remaining 20 kcal/mol must arise mainly from the excess of exchange repulsion over charge-transfer stabilization until the "avoided HOMO–LUMO crossing" occurs.

According to MINDO/3, only 26.5 kcal/mol is required to distort the three acetylenes into the geometry just prior to the transition state (point 8). The remaining 46.4 kcal/mol of destabilization arises from repulsive interactions between the three distorted acetylene molecules. Although MINDO/3 and STO-3G are in close agreement as to the energy of the D_{6h} transition state, the very different partitioning of energy between distortion energy and repulsion energy suggests that this agreement is largely accidental.

As we have discussed earlier,[18] semiempirical methods which do not include overlap, such as MINDO/3, do not include closed-shell repulsions arising from the overlap of the filled orbitals of two or more molecules. Nevertheless, repulsions between molecules are accounted for through parametrization of the various terms which are included in the calculation. These repulsions do not have the same symmetry dependence as closed-shell repulsions,[18] but do produce the same overall behavior of the acetylene geometries along the reaction surface under study here. One reason that MINDO/3 produces such large repulsions is that this technique underestimates the strength of long-range bonding interactions.[19]

Spanget-Larsen and Gleiter recently reported MINDO/3 surfaces for interconversions of 1,4,7-cyclononatrienes and trishomobenzenes.[20] These calculations, like those reported here, indicate relatively high barriers to thermally allowed, six-electron, pericyclic reactions, and indicate that the transition states for these interconversions, but not the isolated molecules, have homoaromatic character.

Precedents and Consequences

The effect noted here explains the orbital energy changes found by Townshend et al.[9] In early stages of the Diels-Alder reaction, molecular distortions occur until the HOMO-LUMO gap becomes sufficiently small for appreciable interactions to occur. The importance of distortion energies upon mechanisms and rates of thermally allowed pericyclic reaction (not to mention all chemical reactions) is profound. Evans and Polanyi explicitly discussed the role of molecular distortion energy upon bimolecular reactions.[21] As they noted, chemical "inertia" is caused by the necessity for the breaking of chemical bonds in a reaction. This concept was applied in a numerical valence-bond fashion to calculate activation energies for atom transfer and cycloadditions such as the Diels-Alder reaction.[21] Wasserman also applied these concepts qualitatively to a discussion of the activation energy of Diels-Alder reaction.[22]

Fukui has emphasized the fact that the gap between the frontier orbitals of reactants narrows as the reaction proceeds,[23] and the acetylene trimerization described here is one example of that principle. Fukui concentrated on the geometrical changes caused by charge-transfer or HOMO-LUMO interactions, whereas we suggest here that thinking in the reverse direction is often equally revealing. That is, geometrical changes occur in such a direction to allow maximum frontier orbital interactions.

The second-order Jahn-Teller effect method of treating favored pathways for unimolecular reactions as developed by Bader[24] and Salem,[25] and extensively applied by Pearson,[4] also explicitly divides energy changes into those arising from molecular distortions and those arising from stabilizing configuration interactions which occur upon distortion away from the equilibrium geometry. As Salem has noted,[25] energies of various configurations change as molecules are distorted, and reactions will be easiest which not only require energetically easy distortions, but which cause a lowering of excited configurations that are of proper symmetry to mix with the ground configuration. Our previous discussion concentrated on HOMO-LUMO interactions, but equivalently could have focused on the fact that acetylene distortions cause a decrease in the energy of excited configurations, involving promotions from the in-plane π orbitals to the in-plane π^* orbitals. However, these configurations substantially mix with the ground configuration only after appreciable distortion.

Recently, Devaquet et al. pointed out similar effects in excited-state reactions.[26] These authors showed that many allowed reactions have activation barriers due to intended, but avoided, orbital crossings. Such barriers, however, are generally lower than avoided state crossings which occur in orbital symmetry forbidden processes. Nagase and Morokuma recently pointed out the influence of "deformation energy" upon the activation energy of additions to alkenes,[27] and we have shown that the distortion of alkenes and alkynes is more significant for additions of nucleophiles than for additions of electrophiles.[28]

Finally, the energy required for molecular distortions needed to facilitate stabilizing HOMO-LUMO interactions is the origin of the "credibility gap" for concerted cycloadditions suggested by Firestone.[29] That is, Firestone claimed that transition states of thermally allowed reactants, being aromatic, should actually be more stable than reactants! The fact that these pericyclic reactions require appreciable activation energies suggested to Firestone that these reactions must proceed through less favorable diradical intermediates, and the otherwise more favorable concerted transition states must be destabilized or avoided by some yet-to-be-discovered factor. This factor is clearly the distortion energy required to facilitate HOMO-LUMO, or "aromatic", interactions. Isolated molecules preserve their closed-shell electronic structures with some tenacity, and must be appreciably distorted before stabilizing, or bonding, interactions with other molecules can occur.

A number of important general conclusions can be gleaned from the acetylene trimerization surface: (1) frontier orbital treatments can successfully account for relative reactivities of a series of molecules only when distortion energies and orbital energy changes upon distortion are similar in the whole series. For example, frontier orbital treatments of the relative reactivities of alkenes and alkynes toward electrophiles are quite successful, since distortions of these molecules are minimal upon reactions with electrophiles. However, distortion energies of alkenes and alkynes are quite different, and these distortions have different effects on the LUMO energies of these two types of molecules; distortions and orbital energy changes thereupon must explicitly be considered in order to explain the greater reactivities of alkynes toward nucleophiles.[28,30]

(2) Mechanisms of pericyclic reactions may change as the requirement for distortion of reactants changes. For example, the concerted mechanism of Diels-Alder reaction of butadiene and ethylene requires a great deal of butadiene and ethylene distortion energy before appreciable frontier orbital stabilization occurs. A diradical mechanism requires much less distortion, but also is stabilized by much weaker HOMO-LUMO interactions. For this case, the available evidence seems to imply that both mechanisms occur to some extent.[30] For good donor-acceptor pairs of cycloaddends, frontier orbital interactions, which stabilize the concerted transition state more than the stepwise, will occur before much distortion has to develop. As a result, the distortion energy which favors the stepwise mechanism will be small, and the concerted mechanism will be favored.

(3) The introduction of strain into reactants may have orbital energy effects which are at least as important as the alteration in reaction exothermicity which may result from a relief of this strain in the reaction in question. A particular distortion of a π system of a reactant may increase HOMO-LUMO interactions, and may have a specific influence on the energy of either the HOMO or LUMO of a given reactant.[28,30]

The consequences of this work on the possibility of observing neutral homoconjugation are discussed in the next section.

Can Neutral Homoaromaticity Be Observed?

Winstein proposed the concept of homoaromaticity to account for the stability of the solvolytically generated bicyclo[3.1.0]hex-3-yl cation.[31] Homoaromaticity is conceivable in neutral or charged systems which have $(4n + 2)$ π electrons, but in which conjugation is interrupted by one, two, etc., bridges (homo, bishomo, etc.). Extensive synthetic efforts have yielded molecules in which the polycyclic framework enforces overlap between the nonconjugated π systems,[2a] and Paquette has devised a theoretical criterion for homoaromaticity based on a vector analysis of overlap calculated from a knowledge of the particular molecular geometry (X-ray analysis) of the species.[32] Related concepts of bicycloaromaticity,[33] spiroconjugation,[34] and a general prediction of stabilization based on ribbon topologies[35] have been developed. Photoelectron spectroscopy has been used to measure the interaction between filled orbitals of molecules such as triquinacene, C_{16}-hexaquinacene, and other potentially homoaromatic molecules,[36,37] and the relationship between interaction (homoconjugation) and stabilization (homoaromaticity) has been described, neglecting overlap.[38] Haddon has used perturbation theory and Hückel theory to describe homoaromaticity in terms of perturbed aromatic systems.[39]

However, the conclusion of the previous section of this paper is that the interaction between π systems of molecules in equilibrium geometries is destabilizing, since filled–filled orbital interactions are much larger than filled–vacant orbital interactions unless the π systems are grossly distorted from their equilibrium geometries. The destabilizing influence of filled–filled interactions is only revealed when overlap is included. Our considerations lead to a conclusion opposite to previous deductions about homoaromaticity: homoconjugative interactions between neutral closed-shell π systems are destabilizing!

Indeed, recent X-ray crystal structures of molecules designed to maximize homoconjugative interactions have revealed distortions in a direction which minimizes, rather than maximizes, overlap of the π systems.[32,37,40,41]

Nevertheless, certain charged systems do provide some evidence for homoaromaticity. In qualitative terms, this has been described as a result of stabilization by charge delocalization.[2a] In terms related to those described here, this can result from the very low-lying LUMO of cations, which can be expected to interact strongly with the HOMOs of π systems of appropriate symmetry even without distortion. Anions have very high-lying HOMOs, and homoaromatic interactions with neighboring π systems of appropriate symmetry could in principle also be relatively facile, although in such examples difficulties with closed-shell repulsion may be expected.

This explanation for the lack of observable homoaromaticity would, at first hand, seem to eliminate the possibility of observing aromaticity as well! However, the difference between potentially homoaromatic and aromatic systems is related to the behavior of the σ frameworks of these two types of molecules upon distortions which maximize π interactions. Consider, for example, the distortions of triquinacene which would be required in order to provide enhanced charge-transfer interactions between the nonconjugated π orbitals. The energy required to stretch three CC double bonds from their equilibrium bond lengths (1.34 Å) to "aromatic bond lengths" (1.40 Å) is $3 \times 2.6 = 7.8$ kcal/mol, using Allinger's potentials[42] for CC double bond stretching. On a polycyclic skeleton such as triquinacene, such deformation will also require various bond length and angle distortions of the σ framework and, in order for homoaromaticity to be observed, the through-space interaction of the π bonds would have to overcome this distortion energy. A crude order of magnitude estimate of the amount of energy required for this skeletal distortion can be made using Allinger's CCC angle bending potentials.[42] In triquinacene, the carbon termini (e.g., C_3 and C_5) of two double bonds are 2.533 Å apart. To bring these carbons to within 1.40 Å, the benzene CC distance (which would still not give overlap as large as that in benzene owing to the different geometries) requires bending the $C_3C_4C_5$, $C_6C_7C_8$, and $C_9C_1C_2$ angles from the equilibrium values of 113.8° to 61.2°. These distortions would give essentially a diademane geometry and would require over 60 kcal/mol of distortion energy, if no relaxation of the electronic structures were permitted. Even a distortion that reduced the C_3C_5, C_6C_8, and C_9C_2 distances to 2 Å would require 24 kcal/mol, and this estimate neglects other angle distortions and van der Waals interactions which would accompany this distortion. Clearly, for a potential homoaromatic to distort in a direction which increases homoconjugative overlaps, a large price in framework distortion energy must be paid.

For 1,3,5-cyclohexatriene, stretching of three double bonds from 1.34 to 1.40 Å and compressing three single bonds from 1.48 to 1.40 Å requires $3(2.6) + 3(5.1) = 23.1$ kcal/mol. However, this distortion is accompanied by a very large increase in aromatic stabilization due to the excellent overlap of adjacent p orbitals.

In the absence of skeletally imposed alkene distortions, "homoaromatic" interactions are actually destabilizing. This phenomenon is reflected most strikingly in the molecular geometry adopted by C_{16}-hexaquinacene, whose three cyclopentene rings are each puckered outward by 5.4° to avoid closed-shell repulsion.[37]

The criteria discussed above can be applied with comparable confidence to strained σ bond (cyclopropyl) interactions. Thus, the unresponsiveness of trishomo-*cis*$_3$-1,4,7-cyclononatriene-d_6 to *degenerate* thermal rearrangement via a "hexahomobenzenoid" transition state[43] can be traced to an inadequacy of stabilizing interactions in the activated complex relative to the level of structural distortion required.

Although one of us has previously ruled out the likelihood that bona fide neutral homoaromatic character will be uncovered,[37] there would appear to remain one condition under which such interactions may be realized. What is required is an appropriately substituted molecule in which one of the π moieties is substituted by strong donors and another by strong acceptors, such that stabilizing HOMO–LUMO interactions may occur without distortion. For this reason, therefore, future effort in the direction of donor–acceptor substitution may prove rewarding.

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References and Notes

(1) (a) Louisiana State University. (b) The Ohio State University.

(2) (a) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978,** *17,* 106. (b) Berthelot, M. *Ann. Chim. Phys.* **1866,** *9,* 445, 469, 481. *Justus Liebigs Ann. Chem.* **1866,** *139,* 272. Miller, S. A. "Acetylene: Its Properties, Manufacture, and Uses", Vol. I; Academic Press: New York, 1965; pp 476–484. Fields, E. K.; Meyerson, S. *Tetrahedron Lett.* **1967,** 571, and references cited therein. A free-radical chain mechanism has been proposed involving initial bimolecular disproportionation to form vinyl and ethynyl radicals (Back, H. M. *Can. J. Chem.* **1971,** *49,* 2199) or homolysis of acetylene to form ethynyl plus hydrogen (Altschuler, B. N. *Kinet. Katal.* **1974,** *15,* 835). These reactions are endothermic by about 83 and 122 kcal/mol, respectively, but the radical chain mechanism has an overall activation energy of 41.6 kcal/mol.

(3) (a) Barkovich, A. J.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1976,** *98,* 2667. (b) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977,** *10,* 1. (c) Barkovich, A. J.; Strauss, E. S.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977,** *99,* 8321.

(4) A termolecular reaction should be $\sim 10^2$ slower than a bimolecular reaction with the same activation energy: Pearson, R. G. "Symmetry Rules for Chemical Reactions"; Wiley-Interscience: New York, 1976; p 140.

(5) Nutakul, W.; Thummel, R. P.; Taggert, A. D. *J. Am. Chem. Soc.* **1979,** *101,* 770.

(6) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Dewar, M. J. S.; Ritchie, J. W., in preparation.

(7) Houk, K. N. *Acc. Chem. Res.* **1975,** *8,* 361.

(8) For a recent study of contrasting frontier orbital control and charge control behavior within a single structural type, see: Bischof, P.; Gleiter, R.; Taylor, R. T.; Browne, A. R.; Paquette, L. A. *J. Org. Chem.* **1978,** *43,* 2391. Browne, A. R.; Paquette, L. A. *Ibid.* **1978,** *43,* 4522.

(9) Townshend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976,** *98,* 2190.

(10) Bingham, R. C.; Dewar, M. J. S.; Lo, D. L. *J. Am. Chem. Soc.* **1975,** *97,* 1285.

(11) GAUSSIAN 70: Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. QCPE 236. Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969,** *51,* 2657.

(12) McIver, J. W. *Acc. Chem. Res.* **1974,** *7,* 72.

(13) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *Int. J. Quantum Chem.* **1977**, *XII,* 61.

(14) Not all computational methods predict a similar barrier. For example, extended Hückel calculations predict that benzene should spontaneously fragment to three acetylenes without activation: Bloemer, W. L.; Bruner, B. L. *Chem. Phys. Lett.* **1972,** *17,* 452.

(15) Wright, J. S. *Chem. Phys. Lett.* **1970,** *6,* 476. *Can. J. Chem.* **1975**, *53,* 549.

(16) Dixon, D. A.; Stevens, R. M.; Herschbach, D. R. *Discuss. Faraday Soc.* **1977,** *62,* 110.

(17) Thompson, D. L.; Suzukawa, H. H., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 3614.
(18) Caramella, P.; Houk, K. N.; Domelsmith, L. N. *J. Am. Chem. Soc.* **1977**, *99*, 4511.
(19) Gordon, M. D.; Fukunaga, T.; Simmons, H. E. *J. Am. Chem. Soc.* **1976**, *98*, 8401.
(20) Spanget-Larsen, J.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 441.
(21) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11. Evans, M. G.; Warhurst, E. *Ibid.* **1938**, *34*, 614. Evans, M. G. *Ibid.* **1939**, *35*, 824.
(22) Wasserman, A. "Diels-Alder Reactions"; Elsevier: Amsterdam, 1965; pp 74–75.
(23) Fukui, K. *Fortschr. Chem. Forsch.* **1970**, *15*, 1. See especially pp 26–28.
(24) Bader, R. F. W. *Mol. Phys.* **1960**, *3*, 137. *Can. J. Chem.* **1962**, *40*, 1164.
(25) Salem, L. *Chem. Phys. Lett.* **1969**, *3*, 99. Salem, L.; Wright, J. S. *J. Am. Chem. Soc.* **1969**, *91*, 5947.
(26) Devaquet, A.; Sevin, A.; Bigot, B. *J. Am. Chem. Soc.* **1978**, *100*, 2009.
(27) Nagase, S.; Morokuma, K. *J. Am. Chem. Soc.* **1978**, *100*, 1666.
(28) Strozier, R. W.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 1340.
(29) Firestone, R. F. *Tetrahedron* **1977**, *33*, 3009.
(30) Houk, K. N. In "Pericyclic Reactions", Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, and references cited therein.
(31) Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524.
(32) Paquette, L. A.; Wallis, T. G.; Kempe, T.; Christoph, G. G.; Springer, J. P.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 6946.
(33) Goldstein, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 6357.
(34) Simmons, H. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1967**, *89*, 5208. Hoffmann, R.; Imamura, A.; Zeiss, G. D. *Ibid.* **1967**, *89*, 5215.
(35) Goldstein, M. J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193.
(36) Bunzli, J. C.; Frost, D. C.; Weiler, L. *Tetrahedron Lett.* **1973**, 1159. Bischof, P.; Bosse, D.; Gleiter, R.; Kukla, J. J.; deMeijere, A.; Paquette, L. A. *Chem. Ber.* **1975**, *108*, 1218.
(37) Christoph, G. G.; Muthard, J. L.; Paquette, L. A.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1978**, *100*, 7782.
(38) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.
(39) Haddon, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 3608.
(40) Roth, W. R.; Bang, W. B.; Göbel, P.; Sass, R. L.; Turner, R. B.; Yü, A. P. *J. Am. Chem. Soc.* **1964**, *86*, 3178.
(41) Stevens, E. D.; Kramer, J. D.; Paquette, L. A. *J. Org. Chem.* **1976**, *41*, 2266.
(42) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 1637.
(43) Detty, M. R.; Paquette, L. A. *Tetrahedron Lett.* **1977**, 347.

Calculations of Rotatory Strengths in Chiral Chromophores. Sensitivity to Structural Parameters in Dienes

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Abstract: The temperature dependence of the effective conformational distribution of the rotamers of the quasi-axial and quasi-equatorial conformers of the dienic molecule α-phellandrene has been calculated using the Westheimer approach as elaborated in the GEMO procedure of Cohen.[1] With the structural parameters obtained from the energy minimization procedure of this method, modified to restrict the distortion of the nominal double bonds of the diene, the rotatory strengths of individual rotamers have been calculated. Using the Boltzmann weighted distribution at 20 and −150 °C, the calculated values are found to be in excellent agreement with chiroptical measurements at these temperatures. The energy difference between the rotamer-averaged quasi-axial and quasi-equatorial conformations is also found to be in good agreement with the measured value. Three significant conclusions may be drawn from these results: (1) Structural parameters of chiral dienic hydrocarbons obtained by the Westheimer method are suitable for rotatory strength calculations. (2) Although the energy differences engendered are not large, the value 26.2 kcal mol^{-1} rad^{-2} heretofore utilized in the GEMO procedure as the double bond torsional constant does not sufficiently account for the stability of the planar structures of π-bonded carbon atoms when the π bond is part of a conjugated system. (3) The CNDO/S method without configuration interaction appears to be adequate to the task of predicting semiquantitatively the rotatory strength of these conformationally flexible dienes.

Introduction

Both empirical and theoretical attempts have been made to understand the chiral activity of the long-wavelength transitions of the dissymmetric diene chromophore. The successful application of the quantum mechanically derived diene rule to a large number of compounds[2] was followed by the discovery of notable exceptions and the derivation of the empirically derived allylic chirality concept.[3] Recently, a significant advance was made by utilizing the CNDO/S calculations for cyclohexadienes.[4] When applied, however, to the calculation of the conformationally mobile dienic compound α-phellandrene as a particularly exacting test of the method, the result was at best qualitatively correct. We have looked for the origin of the lack of better concordance of theory and experiment for this compound and have found that it resides in the extreme sensitivity of the rotatory strength to the molecular structural parameters. In the course of doing so, several very interesting and significant observations have been made with respect to both the utility of the CNDO/S method for this purpose and to the torsional distortion of π bonds in conjugated dienes.

Methods

Experimental data are taken from previous work as referenced. Values of experimentally observed *reduced* rotational strength are calculated from CD curves directly using the expression

$$[R] = 0.4396 \times 10^2 \Delta\epsilon(\Delta\lambda/\lambda) \qquad (1)$$

[where $\Delta\epsilon = [\theta]/3302$ and $[\theta]$ is the measured molar ellipticity, $\Delta\lambda$ is 1/2 the bandwidth at $0.368\Delta\epsilon_{\max}$ (or $[\theta]_{\max}$)], or indirectly from ORD curves using eq 1 and the expression

$$[\theta] = A/0.0122 \qquad (2)$$

(where A is 0.01 of the absolute value of the difference between the molar rotation at the peak and trough of the ORD curve).

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