Organic and Biological Chemistry

The Dependence of Conformational and Isomer Stability on the Number of Electrons in Extended π Systems

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Abstract: In radicals and anions of allylic systems and anions and excited states of polyenes, the excess or excited electrons occupy molecular orbitals which may establish partial bonding between sites not bonded in the corresponding cation or neutral ground-state molecule. For example, the highest occupied orbital in pentadienyl anion is 1,5 bonding and could be expected to stabilize a U-shaped carbanion; similarly in the radical cation, radical anion, and first excited state of butadienes s-cis conformations should be stabilized relative to the s-trans. Extended Hückel calculations indicate that the contribution of the new partial bonding is of the same order of magnitude as the original cation or neutral molecule conformational preference. Simple symmetry arguments show that a methyl substituent essentially plays the role of an added double bond and provide an alternative explanation of the inferred greater stability of cis-methyl allyl anions. The calculations also show that the methyl allyl anions should be conformationally more stable than the corresponding cations. The symmetry arguments yield some interesting fundamental differences among cyclic homoconjugated olefins and allylic anions and cations.

In this paper we wish to present some correlations between conformational and isomer stability and the number of electrons in extended π systems derived from simple molecular orbital arguments and more detailed calculations of the extended Hückel type.[1] From the outset it should be made clear that for each of the phenomena we attempt to explain there exist one or more alternative explanations which we cannot rule out at this time, and which indeed sometimes may prove to be equivalent to our argument.

The "nonbonding" π molecular orbital of pentadienyl has the familiar form I.[2] This orbital is 1,5 bonding; thus there will be a net stabilization if centers 1 and 5 are close enough for their $2p_z$ orbitals to overlap significantly, subject of course to steric restrictions on their proximity. If one, or better two electrons are placed in this orbital to form the pentadienyl radical or anion, it follows that of the three idealized planar configurations of pentadienyl ("U" (II), "sickle" (III), "W" (IV)) II should be preferred to III and IV.[3]

I

II   III   IV
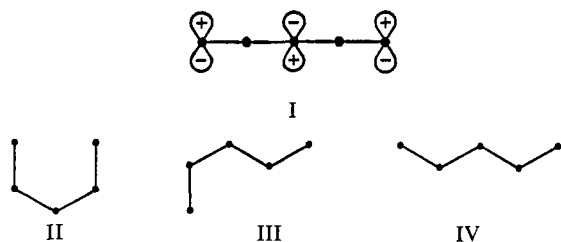
There is some evidence from base-catalyzed equilibrations of the appropriate olefins that the U form is in-

deed stabilized[4] and two possible explanations were offered: one essentially equivalent to the above argument, the other involving stabilization of the chelate form metal–anion ion pairs formed from the U-shaped anions.

For heptatrienyl the nonbonding orbital has the form V. The direct bonding interactions are 1,5 and 3,7

V
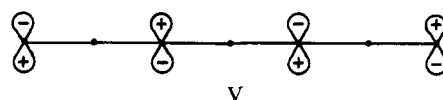
while 1,7 is antibonding. However, there exists in a chain this long the possibility of a gradual helical folding which would not disrupt greatly the π system, but which might allow the bonding interaction of the top of orbital 7 with the bottom of orbital 1 (VI).[5] We have as yet no theoretical or experimental basis on which to evaluate the relative advantage of such a "helical" 1,7 as compared to an in-plane 1,5 interaction. Of the ten distinct planar configurations of heptatrienyl, one would anticipate that the favored anion geometries would be the helical all-cis form VI and the "U-sickle" and "U-W" forms VII and VIII.


VI

(1) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers.

(2) *E.g.*, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 51, 58.
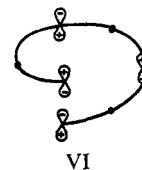
(3) The 1,5 centers are sufficiently far apart in both III and IV so that the stabilizing interaction is negligible for both, and one would not anticipate any difference in the π contribution to their relative energy.

(4) R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3031 (1963). These authors studied the base-induced isomerization of hexahydronaphthalenes and concluded that "U-shaped pentadienyl carbanions are more stable than other planar types with similar substitution by about 2–5 kcal/mole."

(5) Arguments have been given for this type of interaction in the calciferol–precalciferol equilibrium: R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 2511 (1965).

VII   VIII
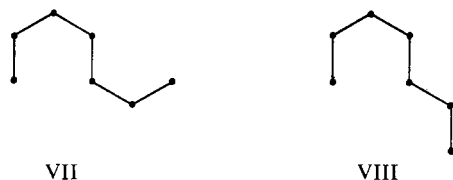
In the pentadienyl dianion radical and trianion, the further extra electrons would occupy an antisymmetric orbital, implying 1,5 antibonding and thus preference of W and sickle-shaped anions over U. This does correspond to the ease of formation of such anions in the 1,5-dioxapentadienyl systems studied by Bauld,[6] but again an alternative rationalization was offered, namely, that the electrostatic interaction of the negatively charged oxygens would favor the W conformation.

Our arguments are easily extended to the excited states of cations and anions. The lowest energy excitation in the pentadienyl cation is from an antisymmetric (A) to a symmetric (S) orbital, implying relative stabilization of the U form in the excited state.[7] The evaluation of the various interactions in all the arrangements of the excited heptatrienyl cation necessitates an analysis of the highest occupied MO, which in this case possesses two nodes. A general result for polyenyl cations is that for planar conformations, $1,4q$ and $1,4q + 1$ interactions are favorable in the excited state; $1,4q + 2$ and $1,4q + 3$ are not ($q = 1,2,\ldots$). Thus for heptatrienyl 1,4 and 1,5 interactions are favorable; 1,6 and 1,7 are not.[8] A more detailed analysis leads to the conclusion that configuration VII is the most favored in the excited state, followed by VIII. A quasi-helical arrangement VI may also be "good," but again we have no grounds on which to compare it to VII and VIII.

These arguments may be relevant to the interesting cyclizations of polyenyl cations in sulfuric acid studied by Deno and co-workers[9] and Sorensen.[10] The postulated primary process in their studies is the 1,5 cyclization of pentadienyl, heptatrienyl, and nonatetraenyl cations to cyclopentenyl derivatives. This cyclization may be classified as an electrocyclic reaction and has been predicted to proceed in a conrotatory manner in the ground state of the cation.[11] The cyclizations appear to be accelerated by light,[10] and if the reaction proceeds through an excited state of the cation it should be a disrotatory process. Unfortunately, under the conditions of the reaction, very rapid hydrogen and alkyl shifts have so far prevented the elucidation of the stereochemistry of the ring closure. The interesting fact still remains that in the longer chain polyenyl cations only 1,5 cyclization has been observed. The role of the various torsional barriers in determining the accessible conformations of an initially all *trans* heptatrienyl cation still needs to be

analyzed. It is interesting that our calculations make the conformations VII and VIII, ideal for 1,5 cyclization, the favored excited-state geometries. Conformation VI is set up for a conrotatory electrocyclic reaction, which is forbidden in the excited state.

In one instance our calculations appear to be in disagreement with experiment. The diagram below (IX)

IX
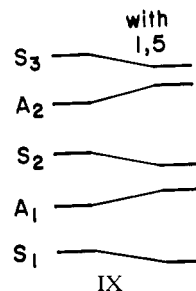
shows in schematic form how the inclusion of a 1,5 interaction affects the position of the pentadienyl energy levels. All A levels are destabilized by such an interaction, all S levels stabilized. We would thus anticipate that the intense long wavelength absorption in pentadienyl cation (presumably $A_1 \rightarrow S_2$) would be shifted to lower energy in "U" compared to "W" geometry; while in the anion the first transition ($S_2 \rightarrow A_2$) should be shifted to higher energy in the "U" conformation. Now there appears to be no information on the former, but there is a careful study on the 1,5-dioxapentadienyl anion spectra by Zaugg and Schaefer.[12] In fact, for the few strictly comparable cases they find that in a U-shaped anion the absorption is shifted to lower energy, opposite to our conclusion. We are at a loss to explain this discrepancy, though assigning spectra from one-electron energy gaps is usually an unreliable practice.

Analogous considerations may be applied to the polyenes. The highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) of butadiene are shown schematically in X and XI. Note that HOMO

X   XI
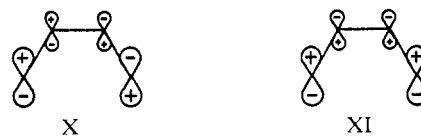
is 1,4 antibonding but LUMO is 1,4 bonding. Thus removing electrons from HOMO (cation), adding them to LUMO (anion), or promoting them from HOMO to LUMO (excited state), all should increase 1,4 bonding and thus stabilize an *s-cis* form relative to an *s-trans*. In the ground state the *s-trans* geometry is the more stable by an imprecisely known energy magnitude in the range of 2–8 kcal/mole. Extended Hückel calculations[1] confirm the stabilization implied by the orbital argument and indicate that in the excited state the *s-cis* and *s-trans* forms should be of very nearly equal energy. There is some experimental support for such a conclusion in the well-known long wavelength shift of the ultraviolet absorption of fixed *cis* dienes relative to similar *trans* dienes. The work of Evans[13] places the triplets of butadiene, isoprene, and cyclohexadiene,

(6) N. L. Bauld, *J. Am. Chem. Soc.*, **86**, 2305 (1964).

(7) An examination of the nodes in the A and S molecular orbitals suggests that 1–2 bonding would be substantially weakened in the excited state, 2–3 not greatly affected. The question whether the excited state remains planar or not and the magnitude of the torsional barriers are being studied. As a preliminary result, it appears that the first excited state of the allyl cation is not planar.

(8) The same 1,2 and 1,3 interactions are present in all conformations of the cation and so they play no role in determining the preferred shape.

(9) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *J. Am. Chem. Soc.*, **87**, 2153 (1965); N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(10) T. S. Sorensen, *Can. J. Chem.*, **42**, 2768 (1964); *J. Am. Chem. Soc.*, **87**, 5075 (1965).

(11) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(12) H. E. Zaugg and A. D. Schaefer, *ibid.*, **87**, 1857 (1965). An isoelectronic system (G. Scheibe, J. Heiss, and K. Feldmann, *Angew. Chem.*, **77**, 545 (1965)) shows a similar trend.

(13) D. F. Evans, *J. Chem. Soc.*, 1987 (1961).

respectively, 59.6, 60.0, and 53.5 kcal above their ground states, implying *cis* and *trans* forms of similar stability in that excited state. The stabilization of *s-cis* anions provides a possible alternative explanation of the results of Bauld,[14] who in studying metal addition to conjugated systems again attributed the observed kinetic control to the thermodynamically less stable *cis* products to tighter ion-pair formation in the *cis* anion.

Similarly in the dications, dianions, radical cations and anions, and excited states derived from the hexatrienes, the 1,4 and 3,6 interactions are bonding, but the 1,6 interactions are antibonding. This implies the following stabilization order

XII
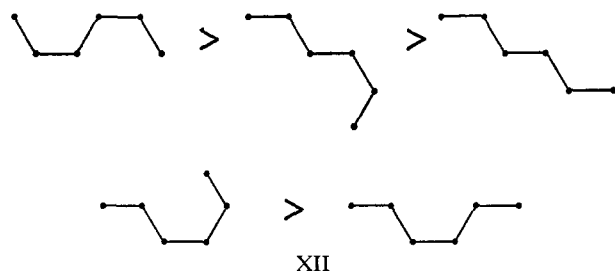
Again the relative position of a quasi-helical arrangement of a *cis*-hexatriene is uncertain in the above ordering. The sequence predicted is in agreement with the known spectra of conformationally fixed hexatrienes.[15] The same order has been also obtained from Pariser–Parr calculations by Allinger and Miller.[16]

The approach is easily extended to other systems. For instance, to evaluate the relative stabilization of the three planar conformations of 3-methylene-1,4-pentadiene, one examines the relevant molecular orbitals,

XIII   XIV   XV
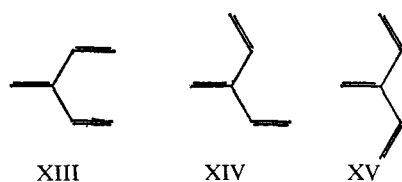
in this case nicely presented by Streitwieser.[17] One concludes that in the ions and first excited state the stabilization order is XV > XIV > XIII. Actually for the related dienones, similar arguments have been used for incipient bonding in the n,π^* excited state.[18]

It is interesting to extend these arguments to the stability of methyl-substituted allylic anions. We wish to examine how the nonbonded allylic orbital is affected by methyl substitution. The CH_3 orbitals interacting with the π system are a C–H bonding combination consisting of a C_42p_z orbital and a π-like H_1–H_2 combination (see Figure 1). (We assume one CH_3 hydrogen in the plane of the anion.)

The nonbonding allyl π will mix in the bonding CH_3 orbital in an antibonding manner (it lies above it in energy), and it will also mix in the antibonding CH_3 orbital in a bonding manner. This type of interaction is, of course, identical with a detailed perturbation

Figure 1. Upper left: orbitals interacting in a methyl allyl species. The CH_3 group is so oriented that one H is in the plane of the allyl group. Upper right: schematic drawing of bonding and antibonding orbitals of the CH_3 group. Middle: mixing scheme for interacting allyl and CH_3 groups. Bottom: mixing of CH_3 orbitals with nonbonding allylic level.

treatment of hyperconjugation. The importance of conjugation effects in an odd system has been stressed by Dewar.[19]

Thus the CH_3 group essentially takes the role of an extra double bond, and the (more-or-less nonbonding) orbital of the composite system looks very much like that of pentadienyl.[20] A consequence of this is again a stabilization of a U-shaped geometry for the anion, *i.e.*, in this case the *cis*-methyl anion is stabilized relative to the *trans* isomer. The accumulating body of evidence for the experimental validity of such a conclusion[21] was indeed the stimulus for this entire study.

The above orbital arguments are abstracted from extended Hückel calculations, which in themselves are not to be trusted for quantitative results. They yield a *trans*-methyl allyl *cation* more stable than *cis* by about 2 kcal, a radical more stable by 1 kcal, and nearly equal stability for *cis* and *trans* anions. The above-mentioned experimental results suggest that actually the *cis* anion is the more stable, but the qualitative results of the calculations appear reasonable.

Calculations were also carried out for a geometry twisted 90° from planarity (of the C skeleton) around the C_2–C_3 axis, with the interesting result that the energy of this unfavorable conformation increased considerably on passing from cation to radical to anion, *i.e.*, indicating that the anions should be conformationally more stable than the cations. The nonbonding orbital, sketched above with zero contribution at C_2, actually has a small component of the wave function at this atom, of the same sign as at C_3; in other words, this orbital is weakly C_2–C_3 bonding, and thus twisting around that bond would be increasingly resisted in the anion.

(14) N. L. Bauld, *J. Am. Chem. Soc.*, **84**, 4345, 4347 (1962).

(15) A. I. Scott, "The Interpretation of the Ultra-Violet Spectra of Natural Products," The Macmillan Co., New York, N. Y., 1964.

(16) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **86**, 2811 (1964).

(17) Reference 2, p 60.

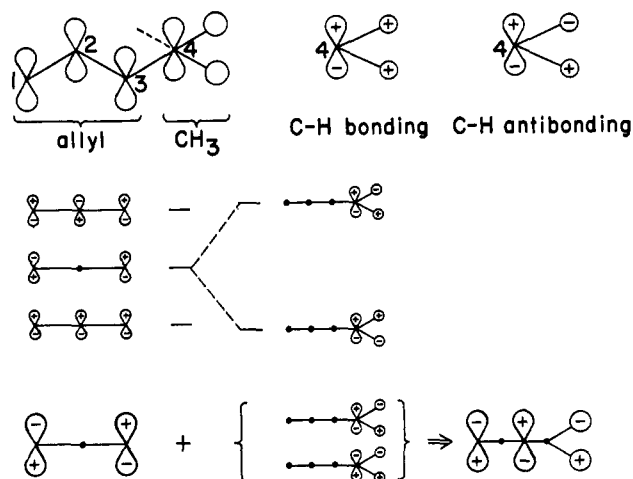(18) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964).

(19) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, p 43.

(20) Entirely analogous analysis of the terminal interaction of a σ orbital with a polyene yields a simple alternative derivation of the important conclusions obtained by K. Fukui, *Tetrahedron Letters*, 2427 (1965).

(21) S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **87**, 3244 (1965), and references therein. An alternative explanation has been forwarded by S. Bank, *ibid.*, **87**, 3245 (1965). We wish to thank Dr. Bank for preprints of these papers prior to publication.

The result is somewhat surprising, and the calculation was repeated for an unsubstituted allyl cation. The torsional barriers vary with the bond lengths assumed for the allylic species, but the qualitative result is very clear: allyl anion is conformationally more stable than the radical which in turn resists twisting more than allyl cation. The individual allylic π levels move in energy with twisting as shown below (XVI). The

XVI
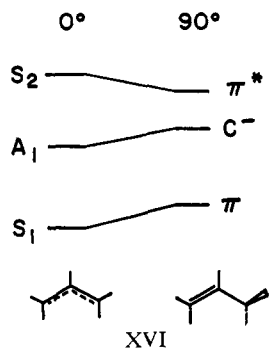
allylic S_1 becomes the π level of the double bond in the 90° twisted geometry, S_2 becomes π^*, while A_1 is transformed into a fairly well-localized lone pair on C_3. In this process the A_1 level increases in energy, and from this derives the greater torsional barrier of the anion. It is still not clear *why* the A_1 level is destabilized by the twisting. Neither is there any experimental evidence bearing on our prediction of the relative conformational stability of allylic anions and cations. From similar calculations we also predict that benzyl anion is conformationally more stable than benzyl cation, but cyclopropylcarbinyl should have a greater torsional barrier than the corresponding anion. Pentadienyl torsional barriers are being studied.

A referee has kindly brought to our attention an example of unusual kinetic control in the metal-ammonia reduction of allenes,[22] particularly the case of 1,2-nonadiene which on reduction yields predominantly *cis*-2-nonene. If the significant intermediate is an allene dianion, then according to some recent calculations[23] such a species prefers to be planar and bent (XVII). The electronic structure of this favored geometry of the allene dianion emerges being very similar to

that of allyl anion; *i.e.*, one can consider in a planar species XVII two electrons approximately localized at

the central atom, and in the plane of the molecule, which leaves four electrons to be placed in an allylic delocalized π system. All of the molecular orbital arguments applied to alkyl allyl anions follow logically, and one concludes that a methyl allene dianion would be most stable as the *cis* conformer of XVIII.

It is of interest to consider the cyclic allylic species XIX and XX, in which a methylene group is interposed between the termini of the π system, and the similar polyenes XXI, XXII, and XXIII. There would appear to be basic theoretical differences in the role played by

the insulating methylene group in various states of these species. Thus the allylic nonbonded orbital has a node which also passes through the methylene group of XIX, while the corresponding pentadienyl orbital has no such node and indeed mixes in the methylene group in XX in a way analogous to that described for methyl allyl; *i.e.*, the final orbital resembles that of benzyl. Similarly the HOMO of XXI and XXIII has a contribution from the methylene group, but not that of XXII. The converse is true for LUMO. One interpretation of these observations is the following: substituents on the allylic system in XX anion will affect the electronic environment and thus reactions of the methylene protons but will have little or no effect in XIX. Conversely, substituents on the methylene carbon would be expected to affect the reactions of the allylic part of the XX anion, but not greatly that of XIX (unless the substituent had low-lying π orbitals, which would reverse the argument). Similar considerations apply to the homocyclic polyenes.

(22) D. Devaprabhakara and P. D. Gardner, *J. Am. Chem. Soc.*, **85**, 648 (1963).

(23) R. Hoffmann, *Tetrahedron*, in press.