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BONDING IN THE MONOHOMOCYCLOOCTATETRAENE ANION RADICAL

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Abstract—We have carried out a series of INDO calculations on the monohomocyclooctatetraene anion radical (MHCOT^{-}). Based upon both the calculated molecular binding energy and comparison of calculated proton hyperfine coupling constants with previously published data, we conclude that the 8-membered ring of MHCOT^{-} is planar. Good agreement was obtained with the experimental hyperfine splittings when the angle between the plane of the 8-membered ring and the plane of the fused cyclopropyl ring was 83·5°. A high π bond order between the carbon atoms at the base of the fused cyclopropyl group strongly supports Winstein's concept of homoconjugation. However, the σ bond orders across the interruption are only reduced by 10–20% relative to the other C–C bonds in the ring, so this bond cannot be considered opened in the anion radical. This is in agreement with the prediction, based on molecular-orbital symmetries, that both disrotatory and conrotatory ring openings are disallowed processes for this species.

INTRODUCTION

The concept of homoconjugation was introduced by Winstein[1] to describe the high stability of molecules and ions in which conjugation is interrupted in one or more places by aliphatic groups. Winstein *et al*[2] view the phenomenon as due to delocalization across the interruption through carbon p-orbitals which are twisted relative to the π orbitals of the remaining system because of the inserted aliphatic group. For the specific case of methylene insertion, Hehre[3] has described how this picture could be rationalized by using the known valence orbitals of the cyclopropane ring.

It is surprising that semi-empirical molecular-orbital treatments of homoconjugated systems have not yet appeared in the literature. To our knowledge, the only pertinent calculations that have appeared are the specially parametrized Hückel-type calculations of Winstein, *et al.*[4] However, since the semi-empirical self-consistent-field all-valence-electron theory of Pople *et al*[5] has been so generally helpful in elucidating molecular structures and properties, we felt it could be advantageously applied to study homoconjugation.

The monohomocyclooctatetraene (or cyclononatetraene) anion radical (MHCOT^{-})[4,6] is one homoconjugated system for which experimental data are directly amenable to comparison with predictions of semi-empirical calculations. The data are the proton hyperfine coupling constants, measured under a variety of conditions by several groups of investigators.[4,6] In our calculations, we sought to match the predicted and experimental hyperfine coupling constants, and thence to examine the nature of the bonding in the MHCOT^{-} from the corresponding wavefunctions.

Our computer program was a slightly modified version of one given by Pople and Beveridge.[5] We used the open-shell (i.e. unrestricted) modification and employed the INDO approximation, with the parameter values suggested by Pople and Beveridge. It should be noted that the calculations provide proton hyperfine couplings directly from calculated spin densities in the hydrogen 1*S* atomic orbitals, and do not involve the use of McConnell's relation[7] or any variation thereof.

The greatest obstacle in the study of such a complex system is the choice of a suitable geometry. The ESR data[4,6] only indicate that the anion radical has a single plane of symmetry, which contains the entire methylene group. The two hydrogens of the methylene group are inequivalent. We have investigated a number of geometries which accord with these observations: a *cis*-fused cyclopropyl connected to an 8-membered ring in a tub configuration, which corresponds to the presumed stable structure of the neutral parent molecule[8] (*cis*-bicyclo[6.1.0]nona-2,4,6-triene); the corresponding *cis*-fused cyclopropyl connected to an 8-membered ring in a chair configuration; and a variety of structures having a planar 8-membered ring with a methylene group in the perpendicular plane of symmetry. For each of these configurations a large number of geometric variables must still be determined. Although we have surveyed the effects of varying some of them, it must be noted that our studies were certainly not exhaustive.

RESULTS AND DISCUSSION

Some of the most pertinent calculated results are listed in Table 1. The results from four calculations are given: the first three are for planar 8-membered rings, as illustrated in Fig 1; the fourth is for the 8-membered tub with a *cis*-fused cyclopropyl group shown in Fig 2. The binding energies, E_B, listed in the table are those obtained from the Pople-Beveridge program.[5] These give the calculated total energy for the species considered relative to the energy of isolated neutral atoms. Since it is

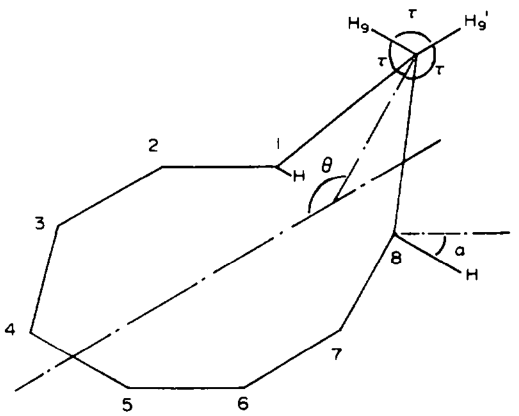

Fig 1. Illustration of the MHCOT⁻ structure with a planar C_8 ring.

well-known that the INDO parametrization gives very poor heats of formation, the absolute magnitudes of these numbers are not meaningful. However, the comparison indicated in Table 1 between planar and non-planar species was typical of all our results. That is, the binding energies clearly indicated greater stability for planar than for non-planar 8-membered rings. This is in agreement with the postulates of the earlier investigators.[4,6]

The experimental proton hyperfine coupling constants[4,6] are listed in the last line of Table 1. It should be noted that we have reversed the assignments of a_H given previously for protons 9 and 9′ in order to improve agreement with the calculations. As stated earlier, our primary concern was to find a structure for which the calculated coupling constants were close to the experimental ones. No structure with a non-planar 8-membered ring could be found to satisfy this criterion. Case (D) of Table 1, which corresponds to the 8-membered tub illustrated in Fig 2, was typical.

The calculation that provided the best comparison between calculated and experimental coupling constants was case (A) listed in the first line of Table 1. This structure was a uniform octagonal plane (Fig 1) with C–C bonds of length 1·40 Å. The out of plane C_1C_9 and C_8C_9 bonds were set at 1·54 Å, and all C–H bonds were assumed to be 1·084 Å long. The C–H bonds at carbons 2–7 were assumed to lie in the plane of the 8-membered ring, bisecting the external C–C–C angles. The hydrogens at C_1 and C_8 were similarly located, but then the C–H bonds were allowed to tilt below the plane by the angle α. In calculation (A), α was equal to 0° and θ, the angle between the octagonal plane and the cyclopropyl ring, was 83·5°. It is interesting that this angle is close to those determined by Hehre[3,9] by *ab initio* calculations on the

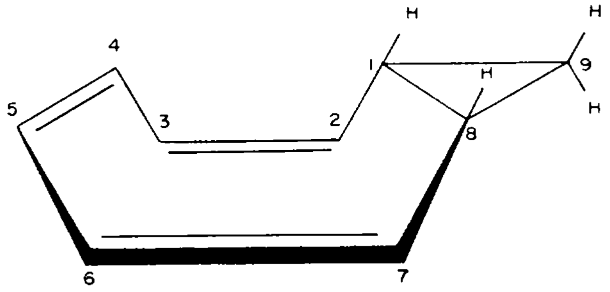

Fig 2. Tub conformation of MHCOT.

Table 1. Proton hyperfine coupling constants

				a_H(G)			
Geometry	E_B (a.u.)	H_1, H_8	H_2, H_7	H_3, H_6	H_4, H_5	H_9	$H_{9'}$
(A) Planar uniform octagon $\theta = 83{\cdot}5°$, $\alpha = 0°$	−9·71	4·21	−1·57	2·62	−2·03	−7·55	−3·71
(B) Planar uniform octagon $\theta = 120°$, $\alpha = 30°$	−9·73	29·91	−5·33	0·62	−2·49	−3·69	−3·17
(C) Planar distorted octagon $\theta = 120°$, $\alpha = 30°$	−9·84	24·75	−5·09	0·66	−2·66	−2·89	−2·97
(D) 8-membered tub with *cis*-fused cyclopropyl	−9·40	27·02	−1·76	26·63	14·73	−3·72	−1·56
Experimental[a]	—	±5·72	±0·87	±5·12	±1·99	±12·18	±4·54

[a] Refs.[4,6]

bicyclo[3.1.0]hex-3-en-2-yl cation and the homotropylium cation.

In case (B) of Table 1, we give the results obtained from the same basic structure as in (A), but with the angles θ and α changed in order to optimize the calculated bindng energy. Calculation (C) is the one that provided the greatest stability based on the calculated binding energy. In this case, the C–C bonds linking atoms C_2 through C_7 were left at 1·40 Å (as in A), but the C_1–C_2, C_7–C_8 and C_1–C_8 distances were increased to 1·49 Å, and some small changes were made in the C–C–C bond angles. Comparisons of cases (B) and (C) with the experimental data illustrate the most problematic aspect of our search: it was extremely difficult to find structures in which the largest calculated hyperfine splitting belonged to one of the methylene protons. Structure (A) was one of the very few investigated for which this was true.

Since structure (A) yielded the best comparison between calculated and experimental hyperfine splittings, the following discussion of the bonding in $MHCOT^-$ utilizes numbers based on that calculation. However, the bond orders obtained from all other structures with planar octagonal rings (in particular, B and C) were very similar. The bond orders were not very sensitive to moderate changes in the bond lengths in the planar octagon.

The calculations were done with the common convention of using a uniform right handed coordinate system throughout the molecule. In the planar structure we therefore have one p-orbital on each carbon which is oriented perpendicular to the plane of the ring. Since these would be designated as π-orbitals in the absence of the methylene groups, it is of interest to look at the various "π-bond orders" described by these orbitals. For the structure described above, these were:

$$(P_\pi)_{1,8} = 0{\cdot}416; \quad (P_\pi)_{1,2} = 0{\cdot}384; \quad (P_\pi)_{2,3} = 0{\cdot}669;$$
$$(P_\pi)_{3,4} = 0{\cdot}609; \quad (P_\pi)_{4,5} = 0{\cdot}602.$$

We thus have close to aromatic π-bond orders around the entire ring between carbons 2 and 7. The 1,2 and 7,8 π-bond orders are understandably reduced because of the attached CH_2 group. The value, 0·416, associated with the C_1–C_8 bond is surprisingly large, and certainly implies that homoconjugation, as envisioned by Winstein,[1,2] does occur.

To get a more complete picture of the overall bonding, we also obtained Mulliken bond orders for the in-plane components of the C–C bonds. This was done by transforming[10] the orbitals for each C–C pair into a local coordinate system in which the p_σ-orbital of each carbon points toward the other carbon, the p_π-orbitals are perpendicular to the ring as described above, and the $p_{\pi'}$-orbitals are in the plane of the ring perpendicular to the bond. For each pair, C_iC_j, this produces a set of bond-orders, $P_{\pi i,\pi j}$ [designated above as $(P_\pi)_{ij}$], $P_{si,sj}$, $P_{\sigma i,\sigma j}$, $(P_{\sigma i,sj} + P_{si,\sigma j})$, $P_{\pi' i,\pi' j}$, which are invarient to the coordinate system used in the calculation.

For the C_1–C_8 bond, we find in general a 10–20% reduction in the σ-bond orders relative to other bonds in the ring. The values of $P_{S1,S8}$, $P_{\sigma 1,\sigma 8}$ and $(P_{\sigma 1,S8} + P_{S1,\sigma 8})$ were 0·270, 0·477 and 0·896, compared to corresponding values of about 0·34, 0·51 and 1·07 for the other C–C bonds. For the π' components, we calculated values of close to $P_{\pi' i,\pi' j} = 0{\cdot}26$ for all pairs of adjacent carbons in the ring, including C_1 and C_8. From these numbers, we must certainly conclude that the strength of the total C_1–C_8 bond is somewhat reduced relative to the other bonds in the ring (perhaps by *ca* 20%). But we cannot conclude that this bond has been "opened" upon formation of the anion radical. If ring opening occurs during the reduction process, we must conclude that it primarily occurs upon addition of the second electron to form the dianion.

This conclusion is in good agreement with the rationalization of the cyclopropyl ring-opening process on the basis of molecular-orbital symmetries. If the symmetries of all occupied orbitals in both the starting material and the products are considered, the orbital correlation diagrams[11] definitely predict that both disrotatory and conrotatory ring openings of the cyclopropyl ring in the $MHCOT^-$ are disallowed processes, since the symmetries of the starting material and the product are different. However, similar considerations lead to the conclusion that the dianion may undergo a symmetry allowed disrotatory cyclopropyl-ring opening process. Once obtained this ring-opened dianion is then capable of establishing an equilibrium between the radical anion and the dianion.

The π-bond orders mentioned above suggest the applicability of a purely π-electron treatment, such as the one used previously.[4] It is therefore interesting to compare the π-orbital spin densities from our calculation with the published values. For $(\rho_\pi)_i$ (i = 1, 2, 3, 4), Winstein *et al*[4] calculated, by Hückel calculations allowing for twisting, 0·1675, 0·0770, 0·1547 and 0·0974. Our ρ_π in the same order were −0·0400, 0·2814, −0·0586 and 0·1171. These two sets are quite different, in regard both to magnitude and to relative values within each set. Recall that this is in spite of the fact (Table 1) that our assigned hyperfine splittings were the same as theirs for the protons attached to C_1 through C_8. This implies (a) that a π-electron treatment of homoconjugated systems is probably not justified, and (b) that McConnell's relation is apparently not applicable in such systems.

CONCLUSION

The significance of the present results are fundamental to a theoretical understanding of the concept of homoconjugation, since they lead to substantiation of the results obtained from consideration of the conservation of orbital symmetry and at the same time establish a mechanism by which the experimental results obtained may be rationalized. In the specific case discussed in this paper, the $MHCOT^-$, the reduction in strength of the C_1–C_8 σ bond by only 20%, compared to a fully formed C–C σ bond, is enough to explain the observed hyperfine coupling constants for the protons attached to C_1 and C_8 and the protons attached to C_9. Pictorially this type of delocalization and in fact the whole concept of homoconjugation has manifest itself among organic chemists as dashed-lines between carbon atoms. Utilization of these dashed-lines to indicate partial bond formation and cleavage can now be firmly grounded in theoretical terms, but it should be thoroughly understood that these dashed-lines do not imply complete delocalization and complete reduction of σ bond strength.

We feel this partial reduction of σ bond strength may be the mechanism by which the stabilization of many other charged species could be explained, and to this end we are currently investigating several carbonium ions and carbanions which are reported to be stabilized by homoconjugation. The most interesting question we hope to answer is what are the limits of this reduction in σ bond strength that can still lead to delocalization and homoconjugative stabilization.

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