

Model Calculations on the Geometry of the Benzene Proton σ -Complex and Its Relation to the Mills-Nixon Effect

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According to CNDO/2 and INDO calculations, the benzene proton σ -complex is stabilized by an appropriate alternation of the C-C bond distances in qualitative agreement with predictions based on simple π -electron theories. Analogous calculations on the benzocyclobutene proton σ -complexes show that the complex is far more stabilized by this bond distance alternation when the saturated bridge is fused to the positions 3 and 4 than when it is fused to the positions 2 and 3. This result is discussed in relation to the qualitative theories which have been put forward to explain the Mills-Nixon effect.

The σ -complex is an important intermediate of ordinary electrophilic aromatic substitution reactions. It has been used successfully as a model for the rate-determining transition state of these reactions. Some of its structural features may be visualized by using simple resonance theory (Fig. 1). The σ -complex is formed in a process in which one pair of electrons of the original stable π -electron sextet of benzene is localized in one new σ -bond. In order to get a more complete description of this structure it is therefore necessary to take into consideration both σ - and π -electrons.

From the bond orders derived from simple resonance or HMO theories, it may be predicted that the C-C bond distances in the benzene σ -complex should alternate. This alternation should be important in systems where a benzene ring is fused to other rings. Recently Vaughan *et al.* have offered the argument of this bond distance alternation in the σ -complex as a qualitative explanation of the predominant ar- β substitution of strained benzocycloalkenes,

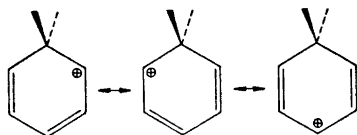


Fig. 1. Resonance structures of benzene σ -complex.

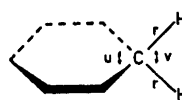


Fig. 2. Benzene proton σ -complex.

i.e. the Mills-Nixon effect.¹ For ar- α substitution the alternation should lead to a shortening of the bond common to the two rings in the benzocycloalkene, and for ar- β substitution the same alternation should lead to a lengthening of the common bond. If one assumes that a shortening of the common bond leads to an increase of the strain in the fused cycloalkane ring, the transition state for ar- α substitution will be destabilized relative to the transition state for ar- β substitution.

It seemed interesting to perform some model calculations on the alternation of the C-C bond distances in the benzene proton σ -complex and by the same method study the importance of this alternation on the relative stability of the ar- α and ar- β proton σ -complexes of a typical strained benzocycloalkene, *i.e.* benzocyclobutene. The CNDO/2 and INDO all-valence-electron methods should be suitable for these calculations.^{2,3}

CALCULATIONS ON THE BENZENE PROTON SIGMA-COMPLEX

The symmetrical benzene proton σ -complex with an unperturbed benzene ring geometry was used as the starting point. The geometric parameters which define the CH₂ group of this model are given in Fig. 2. A CNDO/2 treatment of this model is included in a previous paper.⁴ For u equal to 120° one gets v equal to 101.5° using the hybridization relation. The result of the previous CNDO/2 calculation and a new INDO calculation of the energy as a function of the C-H distances, r , is given in Fig. 3. The CNDO/2 and INDO methods give nearly the same value of r at the energy minima, *i.e.* 1.135 and 1.137 Å, respectively. These values were used as geometric constants in the following CNDO/2 and INDO calculations.

Without aiming at an absolute energy minimum, a simple symmetric alternation of the C-C bond distances was made, starting from the unperturbed benzene ring geometry. The procedure used is indicated in Fig. 4. The bond b is displaced outwards from the center of the structure to a new position

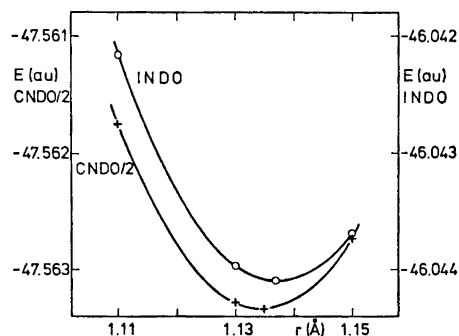


Fig. 3. Energy of benzene proton σ -complex for different carbon-proton distances.

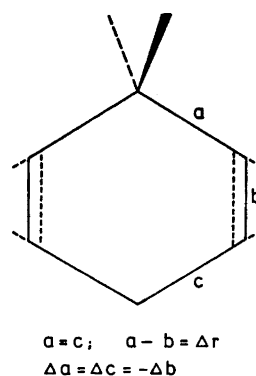


Fig. 4. Perturbation of the benzene ring geometry for a symmetric alternation of the C-C bond distances.

parallel to the original one, while the bonds *a* and *c* are only lengthened. In order to preserve the symmetry, the bonds opposite of *a*, *b* and *c* are replaced in the same manner. During this procedure all intraannular angles are thus kept unchanged at 120° . According to Fig. 4 one may define an alternation parameter Δr , which is equal to the difference between the long and the short C–C bond distances. Calculations were carried out for different values of Δr and the result is given in Fig. 5.

The two methods give similar results, although the absolute energy scale differs for the two. The Δr values at the energy minima are 0.046 \AA by the CNDO/2 and 0.050 \AA by the INDO method. The energy minima lie 4.0 and 4.6 kcal/mol, respectively, lower than the energies obtained for the unperturbed benzene ring geometry.

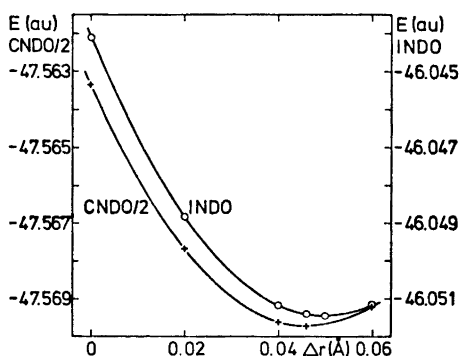


Fig. 5. Energy of benzene proton σ -complex as a function of the alternation of the C–C bond distances.

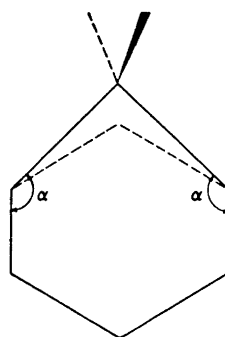


Fig. 6. Final perturbation of the benzene ring geometry involving the length of the two C–C bonds adjacent to the protonated carbon atom.

One simple geometric refinement of the previous treatment of the benzene proton σ -complex was finally made. It consisted of a symmetric lengthening of the two C–C bonds adjacent to the protonated carbon atom keeping the other C–C bonds unchanged in length and position, and starting with the geometry corresponding to the energy minima in the previous calculations. The procedure used is indicated in Fig. 6. In this treatment the angle α , defined in Fig. 6, is made larger than 120° so that the angle u defined in Fig. 2 and determined by α , becomes less than 120° . The geometry of the CH_2 group was kept as before, with the exception of the angle v , defined in Fig. 2, which was derived from the actual value of u using the hybridization relation. The result of the calculation of the energy as a function of α is given in Fig. 7. The decrease in energy which results from this final perturbation is relatively small, being 1.0 kcal/mol by the CNDO/2 and 1.5 kcal/mol by the INDO method. These values correspond to a lengthening of the two C–C bonds adjacent to the protonated carbon atom by 0.019 \AA and 0.023 \AA , respectively.

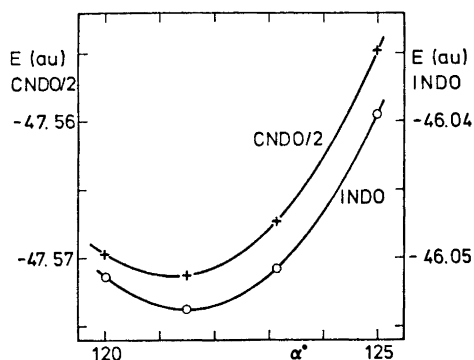


Fig. 7. Energy of benzene proton σ -complex as a function of the final perturbation (increasing the angle α).

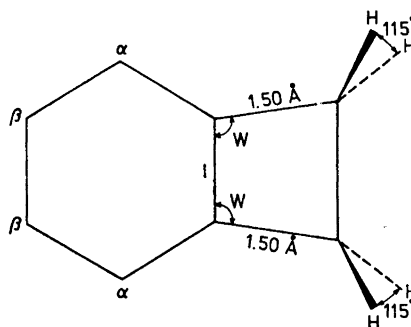


Fig. 8. Benzocyclobutene.

CALCULATIONS ON THE BENZOCYCLOBUTENE PROTON SIGMA-COMPLEXES

The simple symmetric alternation of the C-C bond distances in the benzene proton σ -complex, as outlined in Fig. 4, was applied to the benzocyclobutene σ -complexes. These calculations were performed without any variations of the angle α according to Fig. 6. All interior angles of the benzene ring are thus equal to 120° . Since it was found above that the CNDO/2 and the INDO methods gave essentially the same result, only one of them, the CNDO/2 method, was used here. The structure of benzocyclobutene is shown in Fig. 8. The cyclobutene ring was assumed to be coplanar with the benzene ring and its geometry is determined by l , w and the explicitly given C-C bond distances. The latter were assumed to be the same as the corresponding distances found in benzo[1,2:4,5]dicyclobutene.⁵ The plane of the CH_2 groups of the cyclobutene part was taken to bisect the corresponding exterior C-C-C angles. The angles between the C-H bonds of the CH_2 groups have been roughly estimated considering the small interior angles of the cyclobutene ring. The σ -complexes are formed by the addition of one proton at the ar- α and ar- β positions. The geometry of the benzene ring including the protonated carbon atom was treated in exactly the same way as above for the benzene proton σ -complex according to Fig. 4. The application of the simple symmetric alternation procedure will have different effects on the ar- α and the ar- β proton σ -complexes. In the ar- α proton σ -complex the distance l in Fig. 8 corresponds to b in Fig. 4, while in the ar- β proton σ -complex l corresponds to c . Thus the alternation as outlined in Fig. 4 leads to a decrease of l in the ar- α proton σ -complex and an increase of l in the ar- β proton σ -complex.

A certain geometric optimization of the cyclobutene ring could be accomplished by varying the interior angle w for each specified value of l until an energy minimum was obtained. This optimization was carried out by fitting an adequate number of calculated energy values to a third degree polyno-

mial, from which the energy minimum and the corresponding optimum value of w could be determined. As shown in Fig. 9 the optimum value of w was to a good approximation the same linear function of l for both σ -complexes. Using this relation, the energy of the ar- α and ar- β proton σ -complexes of benzocyclobutene was now calculated as a function of l , the latter being determined by the alternation parameter Δr . The result is given in Fig. 10. The energy difference between the ar- α and ar- β proton σ -complexes at the curve minima is 8.3 kcal/mol. Without any alternation, this difference is only 2.6 kcal/mol. For the ar- α proton σ -complex the energy minimum corresponds to a Δr value of 0.035 Å, while for the ar- β proton σ -complex the energy minimum corresponds to a Δr value of 0.065 Å.

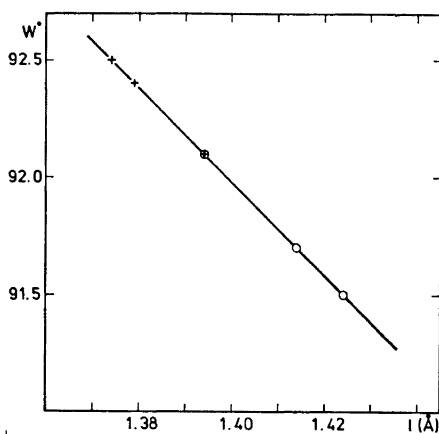


Fig. 9. Optimum values of the angle w of the cyclobutene ring as a function of the length l of the ring juncture bond in benzocyclobutene. Calculated values for the ar- α and the ar- β proton σ -complexes are denoted by + and O, respectively.

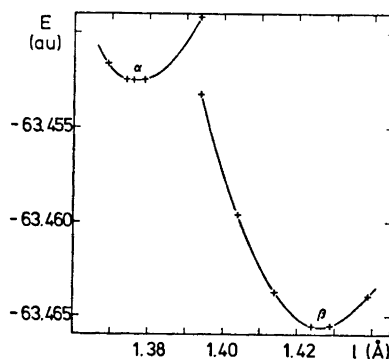


Fig. 10. Energies of the ar- α and ar- β proton σ -complexes of benzocyclobutene as a function of the length l of the ring juncture bond, assuming a symmetric C-C bond distance alternation in the benzene ring.

DISCUSSION

The CNDO/2 and INDO methods used here do not give very good absolute geometries but should be adequate for relative comparisons between structures containing the same type of bonds.⁶ Although several geometric refinements of the present simple treatment of bond distance alternation are possible, it seems probable that the major stabilization effects of this alternation have been accounted for. A more complete treatment should involve independent variations of all geometric variables.⁶ However, such a procedure is extremely time-consuming.

In the case of the benzene proton σ -complex, the geometry obtained substantiates the qualitative predictions of the simple π -electron theories based

on bond-order arguments. Considerations of this type of geometry should be of importance in more accurate calculations on aromatic substitution, especially when the influence of annelated rings or bulky substituents at different positions of an aromatic nucleus is sought.

The behavior of the ar- α and ar- β proton σ -complexes of benzocyclobutene agrees qualitatively with that predicted by Vaughan *et al.*¹ The result given in Fig. 10 may be rationalized by decomposing the curves into two parts. One part consists of the effect of the alternation parameter Δr , directly derivable from l , on the energy of the benzene ring. This effect should be similar to the one demonstrated for the benzene proton σ -complex according to Fig. 5. The other part is then the effect of l on the conformational energy of the fused cyclobutene ring. Apparently, for the ar- α complex the favorable decrease in the energy of the benzene ring, caused by an increase in the alternation parameter Δr , corresponding to a decrease of l in Fig. 10, is partly neutralized by an unfavorable increase in the conformational energy of the fused cyclobutene ring. For the ar- β complex an increase in Δr corresponds to an increase in l and the effects on the energy of the benzene and the cyclobutene ring are both favorable as reflected in the deep curve shown in Fig. 10. It should be noted that the present investigation was only aimed at a demonstration of the effects of symmetric bond distance alternation on the energy of the proton σ -complexes of benzocyclobutene. In order to get quantitative information with regard to the relative reactivities of the ar- α and ar- β positions, more accurate models of the transition states should be used, including considerations of solvent effects. The only kind of electrophilic substitution of benzocyclobutene investigated so far seems to be protodesilylation. Bassindale *et al.* found that the ar- β position was protodesilylated ten times faster than the ar- α position.⁷

Since the present investigation supports the hypothesis put forward by Vaughan *et al.*, it seems appropriate to comment somewhat on an alternative and completely different explanation of the reactivities of the aryl positions adjacent to fused strained rings, given by Streitwieser Jr. *et al.*⁸ Their arguments involve the polarization of the σ -electrons caused by a rehybridization of the orbitals of a ring juncture carbon atom accommodating the small bond angles of a strained fused ring. The net result is a polarization of the σ -electrons away from the ar- α carbon atoms, and using an electrostatic model this leads to a decrease in reactivity of the ar- α positions toward electrophilic reagents. Since polarization effects decrease strongly with distance, the effect on the ar- β position should be much less. The charge distribution in some benzocycloalkenes has recently been calculated by the CNDO/2 method with all geometric parameters optimized.⁹ The total charges of the ar- α and ar- β positions are very small and do not vary significantly among the compounds benzocyclobutene,* benzocyclopentene, and benzocyclohexene. The ar- β positions were slightly more positive than the ar- α positions. These results apparently do not support the polarization argument.

* An independent CNDO/2 calculation on benzocyclobutene using the geometry indicated in Fig. 8 with an unperturbed benzene ring geometry and a simple optimization of the cyclobutene ring through a variation of the angles w gave essentially the same result.

Recently Nilsson *et al.* have studied the directing effects of annelated rings of various sizes in aromatic systems.¹⁰ They found that the five- and seven-membered rings favor bromination in the ar- β position, while the six-membered ring facilitated substitution in the ar- α position. These results are not easily explained either by considering effect on ring strain energies by a bond distance alternation in the benzene ring or by simple polarization arguments. In this case a more complete treatment of all stereochemical features is probably necessary.

Computational details. The main program CNINDO and a subroutine COORD for transforming bond distances and angles to atomic coordinates were obtained through the QCPE service.¹¹ The original atomic parameters proposed by Pople *et al.* were used.^{2,3} All geometric parameters not given in the text or figures were obtained from a standard source.¹² The calculations were performed on a CDC 6600 computer. The points in Figs. 3, 5, 7, and 10, corresponding to actual calculations, could be fitted to third degree polynomials from which the curves with their energy minima were then constructed.

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