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HEATS OF HYDROGENATION

ACEPLEIADYLENE

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Abstract—The heat of hydrogenation of acepleiadylene (**1**) to the corresponding decahydro derivative **5** is −88·35 ± 0·45 kcal/mole, whereas the heat of hydrogenation of acepleiadane to **5** is −29·75 ±0·13 kcal/mole. If the heats of hydrogenation of cyclopentene (−25·7 kcal/mole) and cycloheptene (−25·9 kcal/mole) are used as models to calculate the heat of hydrogenation of the three non-naphthalene double bonds, the value for these three double bonds in such a hypothetical, non-resonating model would be −77·5 kcal/mole in contrast to the experimentally found value of −58·6 kcal/mole. This indicates that the "conjugation" energy of the three non-naphthalene double bonds in acepleiadylene is approximately 18·9 kcal/mole.

ACEPLEIADYLENE (**1**) has long attracted theoretical interest. Isomeric with pyrene, it contains the elements of azulene in which a naphthalene nucleus has been interposed between the 5- and 7-membered rings. As early as 1952, Pullman *et al.*, performed an LCAO–MO calculation of acepleiadylene and predicted such properties as π-electron distribution, bond orders, dipole moment, and electronic transitions.[1] We were able to accomplish the synthesis of acepleiadylene in 1956,[2] and there has been a steady interest ever since in examining its physical properties and comparing them with those predicted from molecular orbital theory.

Pitt *et al.* measured the dipole moment of acepleiadylene and found it to be $0{\cdot}49 \times 10^{-18}$ D,[3] in contrast to the predicted value of $5{\cdot}7 \times 10^{-18}$ D or the empirically-corrected value of $1{\cdot}0 \times 10^{-18}$ D.[1] Didman examined the polarization properties of the electronic transitions of acepleiadylene using a mixed crystal technique with pyrene and found rather good agreement with theory.[4,5]

X-Ray analyses of acepleiadylene and its complex with 1,3,5-trinitrobenzene have been made by Hanson.[6,7] The experimentally-observed bond lengths for acepleiadylene found in these studies are in fair agreement with those predicted for acepleiadylene from the theoretical calculations made by Vasudevan and Laidlaw.[7]

Schneider *et al.* analyzed the proton resonance spectrum of acepleiadylene and made assignments for each of the signals.[8] However, due to uncertainties in the ordering of the nuclei in the AA'BB' and AB systems, Schaefer and Schneider reexamined the ordering on the basis of the calculated π-electron densities.[9] Although

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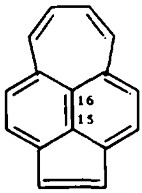
deBoer and Weissman first measured the ESR spectra of the acepleiadylene radical-anion and radical-cation, they could not correlate their observations with theory.[10] Later, Gerson and Heinzer made a detailed study of both the acepleiadylene radical-anion and radical-cation and found good agreement between their experimental spectra and the spin density distribution predicted from an HMO-model.[11]



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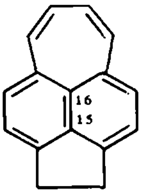

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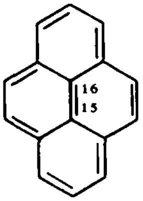

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Of prime interest is the evaluation of the delocalization energy of acepleiadylene and a comparison of this value with that of its isoelectronic isomer, pyrene (3). Grant and Jones have measured the C^{13} magnetic resonance spectra of pyrene[12] and acepleiadylene.[13] The chemical shifts of the peripheral C atoms occur in a rather narrow range for both pyrene and acepleiadylene, suggesting a relatively uniform π-electron distribution in the periphery, whereas the internal C atoms (15 and 16) show a marked upfield shift in comparison with the other quaternary C atoms. This is in contrast to acepleiadiene (2) which, lacking the 14π-electron peripheral system, shows a wider range of chemical shifts and shows signals for carbons 15 and 16 in the normal range for quaternary aromatic carbons.[13] These observations are most readily interpreted in terms of a peripheral ring current and provide strong support for Platt's concept that such molecules will have a stable peripheral π-electron "shell" separated from the inner π-electrons by circular nodes, so that the two loci of unsaturation consist of more or less discrete molecular orbitals.[14, 15]

Dauben *et al.* have used exaltations of the diamagnetic susceptibility as a quantitative measure of "aromaticity".[16] By this test acepleiadylene and pyrene are almost equivalent with the value of $\Lambda_{\text{pyrene}} = 57 \times 10^{-6}\,\text{cm}^3\,\text{mol}^{-1}$ and $\Lambda_{\text{acepleiadylene}} = 53 \times 10^{-6}\,\text{cm}^3\,\text{mol}^{-1}$.[16]

However, the classical approach to determining conjugation energies has been through studies of heats of combustion or heats of hydrogenation.[17] From the heat of combustion of pyrene, Klages deduced that the conjugation energy of pyrene was 108·9 kcal/mole.[18] We have repeated the synthesis of acepleiadylene (with some improvements as noted in the experimental), and measured the heats of hydrogenation of acepleiadylene (1) and acepleiadane (4). From these data it can be deduced that the "conjugation energy" of acepleiadylene is about 80·7 kcal/mole.

The heats of hydrogenation of acepleiadane and acepleiadylene were measured in acetic acid solution at room temperature using platinum oxide as catalyst following the procedure described previously.[19] Although acepleiadylene rapidly absorbs three molar equivalents of hydrogen to give acepleiadane, further reduction of acepleiadane occurs slowly resulting in the uptake of two additional molar equivalents of hydrogen. The ultimate product from either acepleiadylene or acepleiadane resisted further hydrogenation and is assumed to be **5**, although this was not rigorously proven.

The heat of hydrogenation of acepleiadane (**4**) was −29·75 ± 0·13 kcal/mole (average of two experiments, uptake of two molar equivalents of H_2), and for acepleiadylene (**1**) it was −88·35 ± 0·45 kcal/mole (average of two runs, uptake of five molar equivalents of H_2). From these values we can deduce an approximate conjugation energy, which we define as the difference between the observed heats of hydrogenation and the values predicted for hypothetical models having isolated, non-resonating double bonds. Although imperfect, the obvious models to use for making these predictions are cyclopentene for the double bond in the 5-membered ring, cyclohexene for the double bonds in the 6-membered ring, and cycloheptene for the double bonds in the 7-membered ring. The observed values for these heats of hydrogenation are as follows: cyclopentene, −25·7 kcal/mole;[20] cyclohexene, −27·1 kcal/mole;[19] and cycloheptene, −25·9 kcal/mole.[19] Thus, the predicted heat of hydrogenation of **1** → **5** is −133·1 kcal and so the conjugation energy associated with these five double bonds is 133·1–88·4 = 44·7 kcal/mole. If we assume that the remaining benzene ring in **5** has the normal conjugation energy of 36·0 kcal/mole, as assigned to benzene by Kistiakowsky,[21] the total conjugation energy of acepleiadylene is 80·7 kcal/mole.

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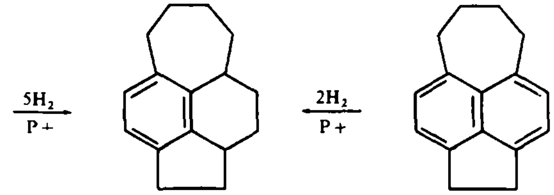

5 **4**

Similarly, the heat of hydrogenation predicted for the transition **4** → **5** would be 2 × (−27·1) = −54·2 kcal/mole. Since the observed value is −29·7 kcal/mole, the conjugation energy associated with the two double bonds involved is 24·8 kcal/mole. If we again assume 36·0 kcal as the conjugation energy of the remaining benzene ring in **5**, the total conjugation energy of acepleiadane is 60·8 kcal/mole, which compares very well with the accepted value of 61 kcal/mole for naphthalene.[18]

By difference, it is readily apparent that the heat of hydrogenation of acepleiadylene (**1**) to acepleiadane (**4**) is −58·6 kcal/mole. Since the predicted heat of hydrogenation of these three double bonds is 2 × (−25·9) + (−25·7) = −77·5 kcal/mole, the conjugation energy of the double bonds in the 7- and 5-membered rings of acepleiadylene is estimated at 18·9 kcal/mole.

The "conjugation energy" by definition is a sum of various terms including π-electron delocalization energy, sigma bond energy,[22] bond compression energy, steric strain energy, etc. Although various arithmetic attempts at separation of these terms have been made, no decisive experimental procedure is available for this purpose. However, the problem of steric strain deserves some comment. With respect to steric strain the conjugation energy of 18·9 kcal/mole for the three double bonds of the 7- and 5-membered rings of acepleiadylene is probably a minimum value. The hypothetical heat of hydrogenation of these three double bonds, given as −77·5 kcal/mole. is undoubtedly too low. The heats of hydrogenation of cyclopentene and cycloheptene are lower than cyclohexene (or *cis*-2-butene) owing to an increase in internal, non-bonded interactions in passing from olefin to paraffin. Since the 5- and 7-membered rings of acepleiadylene possess no tetrahedral C atoms, reduction of the double bonds contained in these rings should result in a product that will be relatively less encumbered by Pitzer strain than is predicted from the cyclopentene-cycloheptene model. Thus, both the hypothetical heat of hydrogenation of acepleiadylene and the conjugation energy derived from it should be higher than the values presented above.

Although the conjugation energy deduced for acepleiadylene from this study is somewhat lower than that credited to pyrene, it is still quite a high value and is in general agreement with the conclusions regarding the "aromaticity" of acepleiadylene arrived at from the magnetic susceptibility and C^{13} magnetic spectral studies.

EXPERIMENTAL

Acepleiadylene I. 1,4-Acepleiadanediol was prepared as described.[23] To a soln of 4·20 g of the mixture of isomers of 1,4-acepleiadanediol (m.p. 140–145°) in 300 ml EtOH ethanol there was added 100 ml saturated soln of HCl in EtOH. The soln turned red immediately and, on standing, it became a reddish-brown. After concentration under reduced pressure, the residue was taken up in a 1 : 10 mixture of benzene-light petroleum (b.p. 30–60°) and chromatographed over neutral alumina. Elution of the main red band gave 2·70 g (75%) of acepleiadiene as brilliant red needles, m.p. 118–119°.

A mixture of 7·0 g acepleiadiene in 180 ml nitrobenzene containing 2·0 g 30% Pd–C catalyst was boiled under reflux for 12 hr. After removal of the solvent under reduced pressure, benzene was added to the residue and the catalyst was removed by filtration. Concentration of the filtrate gave a red solid which was taken up in n-hexane and chromatographed over neutral alumina. Elution of the main red band gave 4·8 g (69%) of acepleiadylene as beautiful red crystals, m.p. 159–161°.

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