# THE NORCARADIENE - CYCLOHEPTATRIENE EQUILIBRIUM

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The equilibrium for the symmetry-allowed interconversion of cycloheptatrienes (1) and norcaradienes (2) generally lies on the side of 1. The existence of such an equilibrium
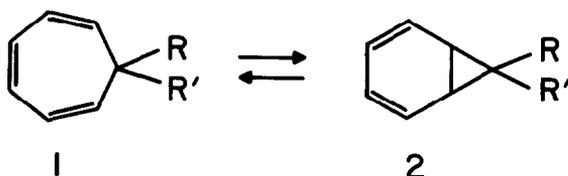
has been demonstrated for the case R = CN, R' = CF$_3$ by Ciganek[1], who also characterized the first simply substituted stable norcaradiene[2], with R = R' = CN. More recently an extensive study of the effects influencing this equilibrium has been made by A. Cairncross[3] for a 2,5-diphenyl substituted cycloheptatriene with R = H, R' varied. An equilibrium constant favoring 2 is found only for R' = ϕ, CN, C≡C-ϕ[4]. A mechanism for this stabilization of 2 by π-electron acceptors is proposed in this work.

Consider the well-established ability of cyclopropane to enter into π-type conjugation with neighboring π-electron systems. When the ligand π-system is a good acceptor, i.e. possesses low-lying unoccupied molecular orbitals, then the important stabilizing interaction is the mixing of the acceptor orbital into the antisymmetric component of the occupied degenerate Walsh orbital pair in cyclopropane[5]. The interaction is shown schematically below.
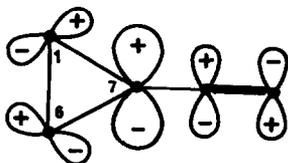
Before interaction the Walsh orbital was occupied by two electrons. After interaction there are still two electrons in the molecular orbital, but now it is delocalized over the vicinal π-system as well. Thus there is net electron transfer from cyclopropane to the π-system. More important for the present case of norcaradiene is that as a consequence of this delocalization 1-6 antibonding is weakened, i.e. the 1-6 bond should become stronger. Similarly the 1-7 and 6-7 bonds should be weakened. The effect should increase with the acceptor strength of the π-ligand, i.e. the lower-lying the unoccupied π-MO of the ligand, the stronger the 1-6 single bond. This behavior is not only consistent with the stabilization of the norcaradiene side by π-acceptor groups such as cyano, but also explains the remarkable cyclopropane bond lengths determined in a very precise crystallographic study of 2,5-dimethyl-7,7-dicyanonorcaradiene[6]. The observed bond lengths are 1.554 and 1.559Å for 1-7 and 6-7 and 1.501Å for 1-6.

Two further molecules which prefer the norcaradiene structure, 3[7] and 4[8], incorporate an external π-electron system rigidly held in the requisite geometry and possessing
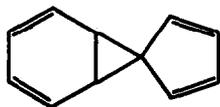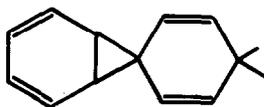
3   **4**

acceptor orbitals of the correct symmetry for the above interaction. Fusion at the 7 position to a cyclopropene or a cycloheptatriene should not favor the norcaradiene form. The analysis proposed here predicts further stabilization of the norcaradiene structure by substituents such as NO_2, NO, and that substituents which are good electron donors would not only destabilize the norcaradiene but lengthen all the cyclopropane bonds.

It is clear that other factors – e.g. substitution sites on the cycloheptatriene ring[2,9,10], external angle at the 7 position[11] – contribute to the observed position of the equilibrium, but I think the dominant factor has been analyzed here.

This work was inspired by a seminar by A. Cairncross, and was aided by some

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3.   A. Cairncross, private communication.

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