

THE INFLUENCE OF FLUORINE-SUBSTITUTION AND PHOTOCHEMICAL ASPECTS OF  
THE INTERACTION OF  $\pi$ -ORBITALS IN THE 1,4-CYCLOHEXADIENE SYSTEM

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Photoelectron spectroscopy shows that the ground state  $\pi$ -energy levels of 1,4-cyclohexadiene and norbornadiene are non-degenerate.<sup>1</sup> The interaction responsible for this splitting takes place *via* space overlap and through-bond coupling, as indicated in analyses of MO-calculations on these systems.<sup>2,3,4</sup> The direct, through-space interaction causes a splitting of the  $\pi$ -energy levels in the positive direction (symmetric combination below *anti*-symmetric). Conversely, the indirect, through-bond coupling causes a splitting of the  $\pi$ -energy levels in the negative direction (*anti*-symmetric combination below symmetric). The balance of these interactions is conformationally dependent: Dominant through-bond coupling in 1,4-cyclohexadiene (dihedral angle<sup>5</sup> 159.3°) causes a large negative splitting (experimental value 1.00 eV<sup>1</sup>). Conversely, space overlap takes precedence in norbornadiene (dihedral angle<sup>6</sup> 115°), which causes a positive splitting (experimental value 0.86 eV<sup>1</sup>).

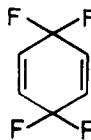
The purpose here is to investigate which factors other than conformational ones may affect the balance of the two modes of interaction in these systems. As has been suggested by Schmidt and Wilkins,<sup>7</sup> fluorine substitution of the  $\sigma$ -system might be expected to reduce the through-bond interaction between two neighboring but formally non-conjugated double bonds without significantly affecting their through-space interaction. Qualitatively, substituting fluorines for the methylene hydrogens in 1,4-cyclohexadiene would be expected to reduce the electron density on the methylene carbon and thus, significantly diminish the interaction between the  $\pi$ -orbitals of the double bonds and the methylene  $\sigma$ -orbital of  $\pi$ -symmetry. This would cause the  $\pi$ -energy levels to come closer and to eventually cross over to a splitting of positive sign.

INDO and HAM<sup>8</sup> calculations on 1,4-cyclohexadiene (1) and 2,2,5,5-tetrafluoro-1,4-cyclohexadiene (2) indicate that the above assumptions are indeed correct. In Table 1, the calculat-

ed splitting of the fluorinated compound 2 is listed for various dihedral angles ( $\theta$ ) and also for comparison of parent 1,4-cyclohexadiene (1) (HAM values parenthesized). It should be noted here that the splitting of 2 is of opposite sign to that of 1 and increases, which is typical of predominant through-space interaction,<sup>3,7</sup> with a decreasing dihedral angle. The magnitude of the splitting in 1 decreases with decreasing dihedral angle, which is in qualitative agreement with the results reported by Dewar and Wasson.<sup>3</sup> In the present study, however, the values calculated according to the INDO method for the splitting in 1 (dihedral angle  $160^\circ$ ) is over-estimated by *ca.* 1.5 eV (experimental value 1.00 eV<sup>1</sup>). Apparently, then, the INDO method either over-estimates the extent of through-bond coupling or underestimates the extent of through-space interaction, or both. Assuming that this is also true for the fluorinated compound 2, the splitting predicted in this case by the INDO method should represent minimal values.



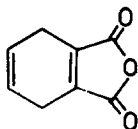
1



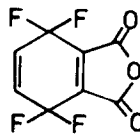
2

Table 1

$\theta$ , deg	180	160	140
$\Delta E$ ( <u>1</u> ), eV	-2.99 (-1.08)	-2.55 (-0.81)	-1.40 (-0.03)
$\Delta E$ ( <u>2</u> ), eV	+0.25 (+0.91)	+0.82 (+1.06)	+1.08 (+1.46)



3



4

Single crystal X-ray crystallography of the 1,4-cyclohexadiene 3 shows that this molecule is almost perfectly planar (dihedral angle<sup>9</sup>  $176^\circ$ ); accordingly, it can be expected to have optimum through-bond coupling. INDO and HAM calculations on 3 based on the molecular geometry from the X-ray study indicate that the  $\pi$ -energy splitting is indeed of negative sign (-2.99 and -1.29 eV, respectively). A similar calculation on the corresponding fluorinated compound 4,

assuming a geometric structure similar to that of 3, predicts that the splitting will be reversed when compared to 3 (+0.25 and +1.03 eV, respectively).

With respect to the different ordering of energy levels in the normal 1,4-cyclohexadiene and norbornadiene systems, it is interesting to note that the photochemical behavior of these systems seems to differ greatly. In the latter system, intramolecular ring closure to quadricyclanes is a general process;<sup>10</sup> conversely, not one example of the corresponding process in the former system has been reported to date. In fact, while 3,4-norbornadienedicarboxylic anhydride undergoes the usual norbornadiene-quadricyclane transformation on irradiation,<sup>11</sup> 1,4-cyclohexadiene-1,2-dicarboxylic anhydride (3) prefers to dimerise.<sup>12</sup>

The sign of the splitting of the ground state  $\pi$ -energy levels seems to have direct bearing on the photochemical behavior of these and related systems: The HAM method gives correct estimates of the excited orbitals.<sup>8</sup> The calculations with this method on the 1,4-cyclohexadiene systems show that a reversal of the ground state  $\pi$ -energy levels is accompanied by a corresponding reversal of the  $\pi^*$ -levels, as indicated earlier by Hoffmann.<sup>2</sup> Thus, in a system with positive splitting the  $\pi$ - and  $\pi^*$ -levels are in order of increasing energy: (SS), (SA), (AS), (AA), while in a system with negative splitting the order is (SA), (SS), (AA), (AS).<sup>13</sup> Intramolecular photochemical ring closure should be possible only when the splitting of the  $\pi$ -energy levels is of positive sign. This principle can be understood in terms of the following: The norbornadiene-quadricyclane transformation should be a direct consequence of the fact that electronic excitation in this case promotes an electron from an orbital which is *anti*-bonding (SA) with respect to the unsaturated *termini* to an orbital which is bonding (AS). The resulting electron configuration is (SS)<sup>2</sup> (SA)<sup>1</sup> (AS)<sup>1</sup>, which constitutes a net gain in bonding between the unsaturated *termini*. In a system with negative splitting, however, a net *anti*-bonding effect between these *loci* is achieved by excitation; the resulting electron configuration, then, is (SA)<sup>2</sup> (SS)<sup>1</sup> (AA)<sup>1</sup>. Examples of the latter effect are the inability of the 1,4-cyclohexadiene 3 and hypostrofene<sup>7</sup> to undergo intramolecular photochemical ring closure. However, it might be anticipated that the fluorinated 1,4-cyclohexadienes 2 and 4 will undergo ring closure to tricyclohexanes on irradiation, since the splittings in these cases are predicted to be positive in sign.

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13. Levels are classified as symmetric (S) or *anti*-symmetric (A) with respect to the mirror planes bisecting the double bonds and the methylene groups, respectively.