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CONSEQUENCES OF A THROUGH-BOND INTERACTION IN TETRACYCLO-[5.3.0.$0^{2,6}$.$0^{3,10}$]-DECA-4,8-DIENE ("HYPOSTROPHENE")*

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Abstract. Photoelectron spectroscopy is used to demonstrate the mechanistic consequences of the level ordering in a given molecule on its reactivity, using the recently synthesized hypostrophene, which contains two CC double bonds in a rigid, cisoid conformation, as an example. The inability of this molecule to close photochemically to the saturated analog is traced to the presence of an exceptionally high-lying σ level which is ideally oriented for an effective through-bond coupling of the two π orbitals. Contrary to the norbornadiene case, this through-bond coupling overrides the direct through-space interaction, placing the in-phase combination of the two π orbitals above the out-of-phase combination, and thus converts the $_{\pi}2_{s}+_{\pi}2_{s}$ photocycloaddition from a symmetry-allowed to a symmetry-forbidden reaction.

INTRODUCTION

IF TWO isolated, non-conjugated CC double bonds are brought face-to-face together, the two π orbitals, described as equivalent in a classical valence bond picture, may split apart energetically as a result of interaction. In molecules like norbornadiene, where the direct through-space mechanism dominates,[2] the in-phase linear combination of the two π orbitals (a_1 within C_{2v}) is placed at lower energies than the out-of-phase combination (b_2); the same holds for the π* orbitals. Facile photochemical ring closure to quadricyclane,[3,4] a wide-spread reaction of norbornadienes, is a direct consequence of this level ordering: electronic excitation promotes an electron from an orbital, which is antibonding with respect to the isolated CC units, to an orbital which is bonding.

The question we attempt to answer in this paper is whether the ordering of the two π levels can be reversed from that postulated for norbornadiene,[5] and if so, whether this has any implications on the course of the photo-induced cycloaddition.

We may anticipate that such a level reversal is most likely to occur by a through-bond mechanism, that is, by interaction with sufficiently high-lying and suitably oriented orbitals of the σ-bond framework.

Although molecules containing small, strained rings are known to possess rather low first IP's,[6,7] they do not appear to be low enough for the condition of a dominant through-bond interaction to be satisfied. We have therefore chosen to look at molecules whose σ framework contains laterally fused three- and four-membered saturated rings. As will be shown below, the coupling of such units produces exceptionally high-lying σ orbitals. When such a σ framework is combined with favourably oriented CC double bonds, the resulting π systems should allow us to subject the current theories about through-space and through-bond interaction to a chemical and spectroscopic test.

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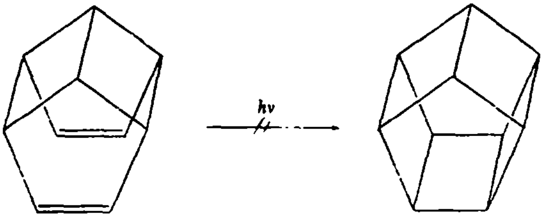
* Photoelectron spectra of delocalized π systems, part 4. Part 3: ref. (1)

RESULTS AND ANALYSIS

A molecule which offers such an opportunity, is the recently synthesized hypostrophene.[8] In this novel $C_{10}H_{10}$ hydrocarbon, which was kindly provided to us by Professor Pettit, two CC double bonds are held in a rigid, face-to-face geometry by a [2.2.0]bicyclohexane moiety. The energetic and stereo-electronic requirements for an efficient through-bond coupling of the two π orbitals are thus ideally met. Below we present evidence that this effect easily overrides the opposed through-space interaction which is furthermore less important in this molecule than in norbornadiene as a result of the increased distance between the double bonds.

A first indication that the ordering of the two π levels is b_2 below a_1 rather than a_1 below b_2 is provided by its inability to undergo the expected ${}_{\pi}2_s + {}_{\pi}2_s$ photocycloaddition to pentaprismane, under any conditions.[9] This puzzling result cannot



be due to thermodynamic instability of the latter molecule: an energy minimization of the geometries of the two species by the MINDO/2 method[10] indicates that pentaprismane should be less stable than its valence tautomer by 26 kcal/mole,* but is protected towards the ${}_{\sigma}2_s + {}_{\sigma}2_s$ cyclo-reversion by a considerable energy barrier, as is consistent with a symmetry-disallowed reaction. Pentaprismane should thus show kinetic stability even at room temperature.

Further arguments in favour of the postulated level reversal arise from the PE spectrum of hypostrophene which is shown in Fig 1.

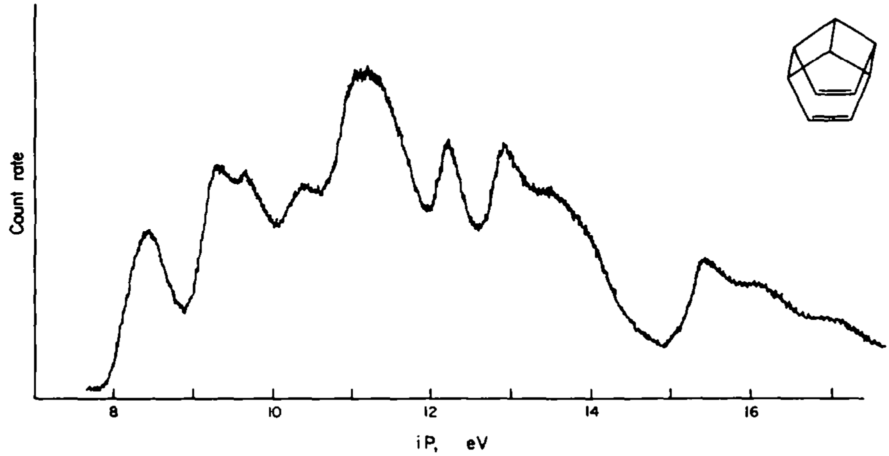


FIG. 1. Photoelectron spectrum of hypostrophene (Perkin–Elmer PS–16 spectrometer).

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* As the MINDO/2 scheme underestimates the ring strain in cyclobutane by 12·3 kcal/mole,[10] a correction of 36·9 kcal/mole was applied to the energy of pentaprismane which contains five 4-membered rings as opposed to two in hypostrophene. An EHT calculation using the MINDO/2 geometries yields a considerable higher energy difference between the two isomers: 81 kcal/mole.

Preceding the ionisations from the σ framework are two distinguishable PE bands, the second of which is split into two components and from its intensity seems to accommodate two ionizations. None of these bands show the steep onset and slow intensity fall-off which is often typical for π ionizations in planar hydrocarbons; this we take to indicate that removal of an electron in each case causes considerable changes in the molecular topography, most probably in the distance between the two CC double bonds. As a consequence transitions to states of the ion with low vibrational quantum numbers are associated with small Franck–Condon factors. Owing to the low frequency of such a bending motion no vibrational structure could be resolved in either of the two bands.

In order to identify the two π ionizations, comparison of the spectrum with a reliable MO scheme is indispensable. As semi-empirical MO procedures have hardly the required accuracy—they appear to be particularly unreliable when σ and π orbitals in non-planar molecules are closely spaced—we shall try to asses the energies of the basic σ and π orbitals before interaction from the IP's of suitable models. Thus from the PE spectrum of ethylene[11] we deduce −10·5 eV for the energy of an isolated CC π level. Similarly the energy of an isolated CC single bond* is determined as −12·1 eV from the spectrum of ethane.[11] In cyclobutane, where the first PE band appears at 11 eV,[7] the highest occupied MO ($3e_u$ within D_{4h}, CC bonding) is found at higher energies as a result of interaction between opposite CC bonds. This shift to higher energies is even more accentuated in [2.2.0]bicyclohexane. Fig 2 shows the wavefunctions of the highest occupied MO's of ethane, cyclobutane and bicyclohexane in an equivalent orbital basis along with the resulting orbital energies; these are expressed in terms of c, the CC self-energy, and e, the interaction element between opposite CC bonds. If we incorporate contributions from lower-lying CH orbitals into the parameter c, we obtain from the PE data of ethane and cyclobutane c = −12·1 eV and e = −1·1 eV and predict the highest occupied MO of bicyclohexane to have an energy of −10·5 eV.

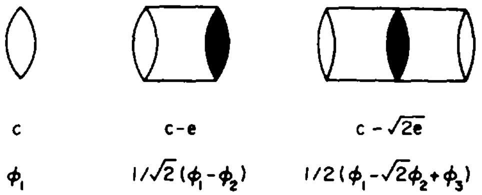

FIG. 2. Schematic representation of the highest occupied orbitals of ethane, cyclobutane and [2.2.0]bicyclohexane in an equivalent orbital basis. The basic EO's are numbered from left to right.

Before interaction, the basic π orbitals and the highest energy bicyclohexane σ level in hypostrophene are thus degenerate and consequently undergo extensive mixing. To predict the splitting between these orbitals, we require a knowledge of the σ–π interaction element and the π–π through-space coupling.

In a recent paper we reported the PE spectrum of *trans*-15,16-dimethyldihydropyrene.[13] The two highest occupied π orbitals, $20a_g$ and $12b_g$, which are symmetry-

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* A re-investigation of the ethane PE spectrum yielded a value of 12·1 eV for the IP of the $3a_{1g}$ level which presents the CC σ bond.[12]

related and thus degenerate in the limits of a D_{14h}-perimeter, were shown to be split by $0{\cdot}4_8$ eV, due to interaction of the former with CC orbitals of the saturated bridge. The parameter, which describes this interaction in a formal way, is of the order of − 1·4 eV. On consideration of molecular models it is immediately evident that the geometrical conditions for σ–π interaction in hypostrophene are of exactly the same type as in *trans*-15,16-dimethyldihydropyrene. We may therefore assume that the through-bond parameter is of the same order of magnitude in the present case. In consequence the splitting of the two orbitals in question would amount to 2–3 eV*. The b_2 π combination, on the other hand, should remain essentially unaffected, unless interaction with unoccupied σ orbitals of the bicyclohexane moiety is invoked.

A rough estimate for the pure through-space coupling can be derived from the norbornadiene PE spectrum which shows two π bands separated by 0·8 eV.[5] This figure represents however only a lower limit to the full through-space effect, as some through-bond coupling also occurs in this molecule.

These estimates, crude as they are, leave however the assignment of the first PE band to the a_1 level beyond reasonable doubt. The strong σ–π mixing deduced above satisfactorily accounts for the apparent broadness and the lack of vibrational structure in this band: ionization induces not only changes in the distance between the double bonds, but also within the σ framework.

Assignments of the b_2 and the other a_1 level to the two components of the second band are less obvious as these are separated in the spectrum by only $0{\cdot}3_5$ eV. It appears, however, that the first component of this band shows a slightly steeper onset than the first band. If we accept the premise that broadness of a band reflects delocalization over the σ framework, we are tempted to correlate the first band component with the b_2 π level, which is essentially free from σ contributions, and the second component with the other a_1 level. The level ordering so obtained would then be in keeping with our deductions about the competitive through-space and through-bond coupling, the latter dominating in hypostrophene. It is also consistent with the MINDO/2 calculations. In the upper half of Fig 3 we have plotted the energies of the three relevant levels as a function of the distance between the CC double bonds, the remainder of the molecular topography being held constant. Through-bond interaction is seen to be the dominating factor for distances larger than 2·3 Å; for smaller distances the π level ordering is dictated by direct through-space coupling. That the latter factor is far from negligible even at 2·85 Å, which is the distance corresponding to the minimum energy conformation, can be confirmed from the lower part of Fig 3, where the energies of the a_1 and the b_2 π level combinations of two approaching ethylenes are displayed as a function of the distance; the two ethylenes are positioned for a given distance in the same way as the double bonds in hypostrophene.

It is somewhat amusing to note that the MINDO/2 as well as the EHT calculations predict for the minimum energy conformation a gap of 0·81 eV between the upper a_1 and the b_2 level; this figure agrees within the limits of accuracy with the observed splitting between the first band and the first component of the second band. Both treatments place furthermore the other a_1 level not far below the b_2 orbital.

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* Strictly speaking, the σ–π interaction depends also on the size of the coefficients at the atoms where through-bond coupling occurs.

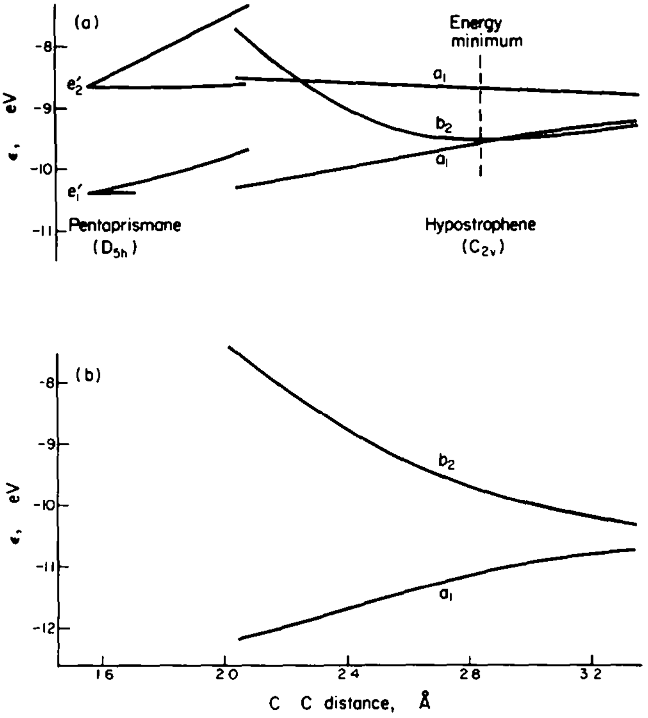

FIG 3. (a) Variation of the orbital energies of hypostrophene (combined through-space and through-bond effect), and (b) of two ethylene molecules (pure through-space interaction) with the distance between the CC double bonds.

Despite this good numerical agreement the level ordering proposed for the second band should be regarded as provisional, pending the results of PE studies on substituted hypostrophenes. An investigations of fluorinated compounds would be illuminating in this respect, as σ bands are known to undergo a shift to higher IP's upon fluorination whereas π ionizations are hardly perturbed.[14] The important feature of fluorine would then be to reduce the through-bond coupling of the two π levels without affecting their through-space interaction significantly. This opens the interesting perspective that the π levels come gradually closer together in energy and eventually cross over, thereby improving the prospects for the photo-cyclization. Efforts directed towards the synthesis of fluorinated hypostrophenes would undoubtedly be a worthwhile albeit arduous project.

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