210. The Electron Affinities of (E)- and (Z)-Cyclooctene[1])

Preliminary communication

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Summary

Electron transmission measurements yield vertical electron affinities of -1.93 eV for (Z)- and of -1.79 eV for (E)-cyclooctene (**Z** and **E**, respectively). It is concluded that the 'out of plane' bending effect in torsioned **E** does not influence its LUMO-energy to a larger degree than its HOMO-energy (as determined by photoelectron (PE.) spectroscopy) with respect to non-torsioned **Z**.

Twisting the C, C-double bond in $R^1 R^2 C = C R^3 R^4$ around the angle θ leads to a decrease of the resonance integral β and therefore to a change of the bonding π-orbital energy [2]:

$$\Delta\varepsilon\,(\pi) \approx 3.6\,(1 - \cos\theta)\ \text{eV} \tag{1}$$

It has been predicted theoretically [3] that this twist is coupled to an 'out of plane'-bending (oop-bend) motion of R^1/R^2 and R^3/R^4 with respect to the original plane defined by the three σ-bonds attached to each of the C_{sp^2}-centers. This motion admixes s-character to the π-basis functions of originally pure $2\,p_z$-type, resulting in a change of the basis energy (effect a) in addition to a change of the resonance integral β (effect b) expressed by *Equation 1*. The 'oop-bend' should therefore manifest itself as a deviation from *Equation 1*, although its explicit incorporation into the equation is not straightforward due to its complex nature.

Photoelectron spectroscopy (PE.) is used to measure approximately the 'experimental' orbital energies *via Koopmans'* theorem. PE. spectra of twisted olefines therefore provided the means to test experimentally the effect of twisting a double bond on occupied orbital energies [2]. The ionization energy (IE.) of (E)-cyclooctene (**E**) was found to lie 0.29 eV lower than the IE. of (Z)-cyclooctene (**Z**). This small change was found to be consistent with *Equation 1* using a torsion

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angle of $\approx 20°$ derived from other experiments. Hence, the consideration of the 'oop-bend' effect was not necessary [2].

A more sensitive test of the effect will be obtained by determining simultaneously $\Delta\varepsilon\,(\pi^*)$. In analogy to *Equation 1*, for a pure twist, we obtain (within the ZO-approximation)

$$\Delta\varepsilon\,(\pi^*) \approx -3.6\,(1-\cos\theta)\ \text{eV} \tag{2}$$

although the numerical value of the resonance integral could be slightly different due to the more diffuse nature of the virtual orbitals [4]. Hence

$$\Delta\varepsilon\,(\pi) \approx -\Delta\varepsilon\,(\pi^*) \tag{3}$$

The equality, however, will be removed if significant 'oop-bend' is operating: no matter how β changes (effect b), the admixture of s-character to the $2p_z$-basis (effect a) will decrease the center of gravity of the π-orbitals, leading to

$$\Delta\varepsilon\,(\pi) < -\Delta\varepsilon\,(\pi^*) \tag{4}$$

The advent of electron transmission spectroscopy (ET.) [5] allows the determination of approximate 'experimental' values of the unoccupied orbital energies. In a manner similar to PE. spectroscopy, *Koopmans'* theorem connects the experimentally determined electron affinity (EA.) with the corresponding orbital energy.

We found vertical electron affinities *(Figure)* of -1.93 eV **(Z)** and -1.79 eV **(E)** which results in $\Delta\varepsilon\,(\pi^*) = -0.14$ eV for the two cyclooctenes. With $\Delta\varepsilon\,(\pi) = 0.29$ eV from [2] we obtain $\Delta\varepsilon\,(\pi) > -\Delta\varepsilon\,(\pi^*)$ in disagreement with *Equation 4* based on the assumption of a significant 'oop-bend' contribution. We conclude in agreement with [2] that the influence of the latter on HOMO- and LUMO-energies appears to be negligible in the present example where $\theta \approx 20°$ **(E)**.

The cosine function in *Equation 1*, which does not differ much from unity for small angles θ explains the relative insensitivity of the PE. and ET. results on small
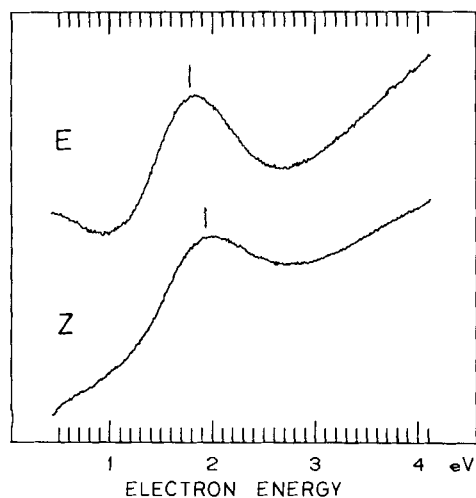
ELECTRON ENERGY

Figure. *ET. curves for (E)- and (Z)-cyclooctene* (**E** and **Z**, respectively)

twists of the double bond. The 'oop-bend' effect appears to have a similar characteristic with respect to orbital energies although, from structural analysis, 'oop-bend' angles of 22°–24° for $\theta = 18°–21°$ have been found [6]. The probability of confirming *Equation 4* would increase if a compound with a more strongly twisted double bond (and therefore probably also with a larger 'oop-bend' effect) than **E** could be investigated. Unfortunately (*E*)-cycloheptene appears to be too unstable for this type of experiments.

Recently, it was found that the $Fe(CO)_4$-complex of **E** is significantly more stable than that of **Z** [7]. From ^{13}C-NMR. and vibrational spectra it was concluded that this outcome is predominantly due to an increased donor capacity of the (*E*)-cycloolefin, improved backbonding from the metal center to the lowered olefin π^*-level being of less importance. This reasoning implicitly assumed a negligible 'oop-bend' effect on the π/π^*-levels of strained **E**. The present results support this interpretation.

We finally mention without further comment that operation of the ET. instrument in the energy-loss mode yielded the following first excited singlet (S_1)- and triplet (T_1)-state energies (vertical values):
- residual e^--energy 20 eV: $S_1(Z) = 6.45$ eV (6.23 eV in hexane [7]),
                    $S_1(E) = 6.31$ eV (6.17 eV in hexane [7]),
- residual e^--energy 0.05 eV: $T_1(Z) = 4.06$ eV,
                    $T_1(E) = 3.76$ eV.

The sequence of S- as well as T-energies for the two isomers are in accord with the expectation based on elementary theory.

Experimental. – The ET. instrument is of the type introduced by *Sanche & Schulz* [8] (*cf.* [5]) and has been described in detail in [9]. The curves displayed in the *Figure* are the negative of the transmitted current, in arbitrary units and with zero offset. The curves represent approximately the total scattering cross sections. The trapping of an electron into an unoccupied orbital to form a short-lived negative ion (resonance) causes an increase in the scattering cross section [5] and appears as a peak superimposed on a monotonous background of direct scattering. Note that our method of presenting the ET. data is somewhat different from the generally used derivative of the transmitted current [5], where the resonance appears as a dispersion curve instead of a peak. The samples were prepared and purified according to [7] [10]. In addition, **E** was also purified by GC.

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