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THROUGH-BOND AND THROUGH-SPACE INTERACTIONS

THE ELECTRONIC SPECTRUM OF BARRELENE

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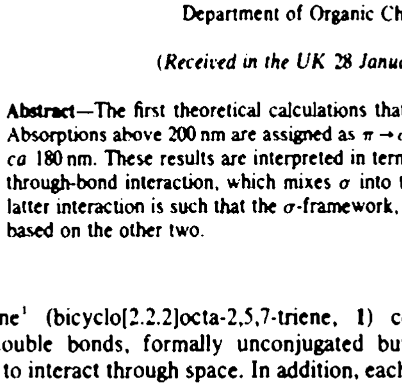
Abstract—The first theoretical calculations that reproduce the observed UV spectrum of barrelene are reported. Absorptions above 200 nm are assigned as $\pi \rightarrow \sigma^*$ while the first excitation that is essentially $\pi \rightarrow \pi^*$ is predicted at *ca* 180 nm. These results are interpreted in terms of through-space π–π interaction, which splits the π-levels, and through-bond interaction, which mixes σ into the π, and fills in the gap between the antibonding π-orbitals. The latter interaction is such that the σ-framework, in each of the three bridges, couples the ethylenic moieties that are based on the other two.

Barrelene[1] (bicyclo[2.2.2]octa-2,5,7-triene, I) contains three double bonds, formally unconjugated but close enough to interact through space. In addition, each of the ethylenic systems is close to σ-bonds with which it is not orthogonal [e.g. 5–6(π) to 1–2(σ), etc.], so that through-bond π–π interactions can also be envisaged. Barrelene offers therefore an opportunity to examine an interplay of interactions between non-contiguous centers of unsaturation.[2]



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The near UV spectrum, in ethanol, has been described[1] as comprising two peaks, 208 nm (ϵ 1,120) and 239 nm (ϵ 320). These do not shift significantly in cyclohexane,[3] where it is revealed that the band near 200 is, in fact, complex, and that an additional feature occurs at 296 nm ($\epsilon < 2$). The photoelectron spectrum has been taken, and vertical ionization potentials located at 8.23, 9.65 (degenerate source orbital), 11.25, 11.9–12.0 eV, and at higher energies.[2]

On the theoretical side, extensive attention has been accorded to barrelene. Geometrical parameters were estimated by molecular-mechanical force fields.[4,5] Numerous MO calculations have been reported, including π-electronic,[1,6,8] σ-induction π-electronic,[9] all valence-electron (MINDO/1,[10] MINDO/2,[2] INDO,[6] extended Hückel[11]) and all-electron[12] treatments. It was found that, although ionization potentials could be assigned,[2] none of those methods that aimed at the calculation of the spectrum led to agreement with experiment—even when results for cognate molecules were representative.[9] Consequently, the structure-dependent roles of σ- and π-electrons, in determining the spectrum of barrelene, still await a quantitative analysis.

We have recently described a semiempirical SCF-CI MO scheme that is specifically oriented towards the computation of spectral quantities.[13,14] Calculations by this method do reproduce the reported absorptions of barrelene, and also predict that the first strong excitation would occur at around 180 nm—coinciding thus with the strong absorption observed[15] in norbornadiene. In what follows, we present our results and the analysis that depends thereof.

Method

The methods used are our π-electron scheme[16] and its extension to the complete C-H structure of hydrocarbons,[13,14] itself a generalization of our semiempirical SCF-CI MO treatment of molecular backbones.[17] Here, the basis-set comprises one 1s-AO for each hydrogen, and four sp^n hybrids at each carbon, with indices n (non-integer) derived from the geometry. The method is analogous, in a way, to Sandorfy's "H-approximation",[18] but is very sensitive to structural detail. Hydrogen-parameters were derived by best-fitting to strong absorptions in the spectra of methane, ethane and propane.[14]

Calculation and results

Previous authors have most frequently assumed a geometry[4] with $r(C{=}C) = 1.337$, $r(C{-}C) = 1.501$, $r(C_1{-}H_1) = 1.095$, $r(C_2{-}H_2) = 1.085$ A, $\theta(H_1C_1C_2) = 113.9°$ and $\theta(H_2C_2{=}C_3) = 123.1°$. We have examined this, and also an alternative geometry, closer to a one recently proposed,[5] in which C–C distances are like in Dewar-benzene,[19] namely, $r(C{=}C) = 1.345$ and $r(C{-}C) = 1.524$ A. A force-field check, using Allinger's constants,[20] yields indeed a somewhat lower energy for the second geometry (0.24 kcal mol^{-1}); in molecular-mechanical terms, the diminished 1,4-repulsions, in the second geometry, outweigh its enhanced bond-stretching strain. The computed heat of formation (70.2 kcal mol^{-1}) is lower than the MINDO/1 prediction[10] (78.0), and corresponds to a strain-energy of 19.3 kcal (previous estimate[10] 23–27). Still, these numbers do not take account of the consequences of π–π interaction. MO results are practically identical in the two geometries.

In a preliminary calculation, only unsaturation orbitals (π-orbitals) were included. The MO's[21] had the following energies (in eV): 3.08 (a_1''), 2.02 (e'', LVMO), −8.72 (a_2', HOMO), −11.43 (e'). By the appropriate regression line,[16] these correspond to ionization potentials of 8.65 and 11.15 eV; of these, the second is appreciably in error.[2] The first computed transitions are at 265 (E'') and 187 nm (A_2''). Clearly, π-orbitals alone do not account for the observed properties of barrelene.

In the main calculation, all valence orbitals—on carbons and hydrogens—were included. The effect of including σ is depicted in Fig. 1, and data on relevant MO's are given in Table 1. A helpful feature of the computational method is that each element in the basis refers to a particular bond, so that each MO can be ascribed to a zone (or zones) within the molecule. These assignments also are marked in the Table: BH denotes a bridgehead carbon (C_1 and C_4), B—a bridge carbon (C_2, C_3, C_5, C_6, C_7, C_8), and H—hydrogen, so that, e.g. BH–B refers to σ-bonds 1–2, 1–6, 1–7, 4–3, 4–5 and 4–8.

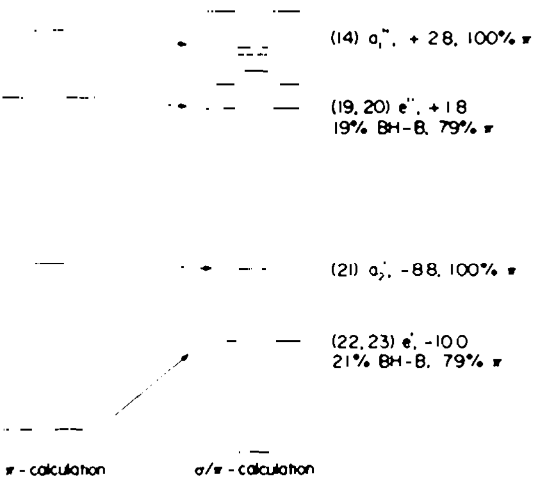

Fig. 1. Fate of molecular orbitals on σ–π interaction. Given: number (as in Table 1), symmetry, energy (eV), type of level.

Table 1. Molecular orbitals of barrelene

No.	Energy (eV) and symmetry (D_{3h})	Main contributions
12, 13	3.4 (e')	38% BH-B, 62% B-H
14	2.8 (a_1'')	100% π
15	2.7 (a_2'')	60% BH-H, 29% B-H
16	2.4 (a_1')	36% BH-H, 61% B-H
17, 18	2.2 (e')	60% BH-H, 40% B-H
19, 20 (LVMO)	1.8 (e'')	79% π, 19% BH-B
21 (HOMO)	8.8 (a_2')	100% π
22, 23	- 10.0 (e')	79% π, 21% BH-B
24	−11.8 (a_1')	mixed
25	−12.9 (a_2'')	71% BH-B, 23% BH-H
26, 27	13.0 (e'')	54% BH-B, 44% B-H

Computed absorption-wavelengths are listed in Table 2. The two transitions, predicted in the preliminary π-electron work (265 and 187 nm), are not affected much when σ-electrons are included. However, it is found now that they delimit a spectral range which contains 13 additional excitations; among these, two are allowed $\pi \rightarrow \sigma^*$ (2 and 6, E'), very close to the experimental maxima. Computed singlet-triplet transitions fall at 361 (E''), 340 (A_2''), 263 nm (E') and shorter wavelengths. The spectral irregularity encountered[1] at 296 nm ($\epsilon < 2$) rests thus unassigned.

Table 2. Computed spectrum of barrelene

No.	λ (nm) and symmetry[a]	Main contribution[b]	Type
1	265 (E'')	21 → 19, 20	$\pi \rightarrow \pi^*$ and $\pi \rightarrow CC^*$
2[c]	247 (E')	21 → 17, 18	$\pi \rightarrow CC^*$ and $\pi \rightarrow CH^*$
3	231 (A_2')	21 → 16	$\pi \rightarrow CH^*$
4	217 (E'')	mixed	mainly $\pi \rightarrow \pi^*$ (e'–e'')
5	214 (A_1'')	mixed	some $\pi \rightarrow \pi^*$
6[d]	209 (E')	21 → 12, 13	$\pi \rightarrow CC^*$ and $\pi \rightarrow CH^*$
7	204 (A_1'')	mixed	mainly $\pi \rightarrow \pi^*$ (e'–e'')
8	203 (A_2')	mixed	$\pi \rightarrow \sigma^*$ (e'–e' and a_2'–a_1')
⋮			
15[e]	181 (A_2'')	mixed, 24% 21, 14	mainly $\pi \rightarrow \pi^*$ (e'–e'' and a_2'–a_1'')

[a] Only E' and A_2'' correspond to allowed transitions.
[b] Numerotation of Table 1.
[c] Allowed but very weak. Expt. max.[1] 239 nm (ϵ 320).
[d] Allowed but weak (f = 0.11). Expt. max. 208 nm (ϵ 1120).
[e] Allowed and strong (f = 0.86). Outside experimentally-scanned range.

DISCUSSION

In the π-electronic calculation, the occupied molecular orbitals are not all degenerate, nor are the virtual. This, in itself, indicates *through-space* π–π interaction.[22] In our construction, the effect is overlap-dependent, although transannular overlaps are comparatively small: 2,3(π), 0.27, but 2,6(π), 0.06 and 2,5(π), 0.03 (in absolute value). Still, through-space interaction—that is, a model with π-orbitals alone—cannot, and does not account for the spectrum of barrelene. In particular, the gap computed between occupied levels (2.7 eV) is too high, as evidenced by confrontation with the ionization potentials, and with the value cited[15] for the corresponding gap in norbornadiene (0.8 eV).

π-Orbitals in barrelene transform as a_1'', e'', a_2', e'; σ-orbitals—as $7a_1'$, $5e'$, $7a_2''$, $5e''$. The sigma network is therefore in position to affect the degenerate, but not the non-degenerate π-levels. Calculation shows (Table 1) that the former mix, to about 20%, with the bridgehead-bridge skeletal bonds (C_1–C_2, etc.). This provides a *through-bond* mechanism for π–π interaction: each pair of bridging bonds "relays" the two ethylenic moieties that are not based on it, e.g. C_1–C_2 and C_4–C_3 (σ) couple C_5–C_6 with C_7–C_8 (π). In fact, some of the $\sigma-\pi$, overlaps exceed the corresponding π–π numbers: $C_1 \rightarrow C_2(\sigma)$, $C_6(\pi)$ 0.14; $C_2 \rightarrow C_1(\sigma)$, $C_6(\pi)$, 0.07; $C_1 \rightarrow C_2(\sigma)$, $C_5(\pi)$, 0.02; $C_2 \rightarrow C_1(\sigma)$, $C_5(\pi)$, 0.02 (in absolute values).

The interaction pushes up the e' π-orbitals, thus narrowing the split between π-levels to a value of 1.2 eV. Also, anitbonding σ-orbitals fill up the gap between the antibonding π-levels. One may remark parenthetically that this double pattern—raising of bonding π and gapfilling in the antibonding—is by no means peculiar to barrelene: it is to be expected in other molecules that contain an unsaturated portion close and properly oriented with respect to a saturated moiety. *Inter alia*, it provides[13] an interpretation of the bathochromic-hypochromic spectral shift observed on passing from piperitone to verbenone.[23]

The only electronic transition which may happen to be pure $\pi \rightarrow \pi^*$ is $21 \rightarrow 14$ (numerotation of Table 1). Yet, this is A_2'', and could mix, e.g. with $22,23 \rightarrow 19,20$ $(A_1' + A_2'' + E')$ which is not pure $\pi \rightarrow \pi^*$. In other words, there is no reason to exclude σ intervention throughout the spectrum, even in an excitation that is predominantly $\pi \rightarrow \pi^*$.

Table 2 shows, indeed, that the two absorptions that are allowed above 200 nm, start at a pure π-MO but terminate at σ orbitals. Their computed location is close to the peaks measured, in ethanol[1] or cyclohexane.[3] Incidentally, it has been suggested that these peaks would shift in the vapor-phase to higher energies.[24] Confrontation with data on norbornadiene does not substantiate such an eventuality: the first vapor-phase peak in the latter molecule, 208 nm,[15] compares by intensity with the ethanol solution peaks[7] at 214 and 205 nm.

The first strong absorption of barrelene is predicted (Table 2) at 181 nm, coinciding thus with the strong absorption observed[15] in norbornadiene. Even this transition is characterized as a configurational mixture, containing only about 75% $\pi \rightarrow \pi^*$.

CONCLUSION

In barrelene, the ethylenic bonds interact both *through-space*, which determines the ordering of those orbitals that are predominantly π, and *through-bond*, which mixes σ with π, and inserts antibonding σ among the antibonding π. As a consequence, no transitions are pure $\pi \rightarrow \pi^*$; those of lowest energy, are $\pi \rightarrow \sigma^*$.

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