The Photoelectron Spectrum of 7b-Methyl-7b*H*-cyclopent[*cd*]indene

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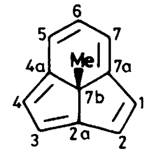
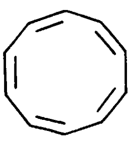
The He^{I} photoelectron (p.e.) spectrum of 7b-methyl-7b*H*-cyclopent[*cd*]indene (**1**) has been recorded. The first four bands are assigned to ionization events from π-orbitals related to the perimeter of [10]annulene. This assignment is based on model calculations using the HMO and the MINDO/3 model. The p.e. spectrum of (**1**) is compared with that of 1,6-methano[10]annulene (**3**). The rearrangement of (**1**) to its 2a*H* isomer (**4**) is also discussed.

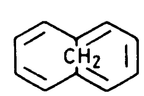
With the synthesis of the tricyclic [10]annulene, 7b-methyl-7b*H*-cyclopent[*cd*]indene (**1**),[1] its electronic structure and reactivity have come into focus. To contribute to these questions we report in this paper the He^{I} photoelectron (p.e.) spectrum of (**1**) and in connection with the interpretation of this we discuss the results of MO calculations on (**1**).



(**1**)



(**2**)



(**3**)

Discussion

*Photoelectron Spectrum of 7b-Methyl-7b*H*-cyclopent*[cd]*indene* (**1**).—Figure 1 shows the He^{I} photoelectron spectrum of (**1**). In the Table we have collected the ionization energies of the first bands in the p.e. spectrum of (**1**). The p.e. spectrum of (**1**) shows three peaks below 10.5 eV, two overlapping bands at 7.5 and 8 eV, and one Gaussian-shape band at 10.0 eV. These signals are followed by a relatively broad peak centred at 11 eV.

If we assign two ionic states to the first peak (bands 1 and 2) it seems reasonable to assign one ionic state to band 3 and probably three ionization processes to the broad band around 11 eV, judging from the area below the envelopes and assuming about equal cross-sections for the first bands.

To interpret the first bands in the p.e. spectrum of (**1**) we apply Koopmans' approximation, which allows us to correlate the measured vertical ionization energies ($I_{v,j}$) with the calculated molecular orbital energies (ε_j) of the ground state,[2] equation (1).

$$I_{v,j} = -\varepsilon_j \qquad (1)$$

Judging from our studies on the p.e. spectra of non-benzenoid aromatic systems[3] and the work on bridged annulenes[4] it seems reasonable to assign the bands below 11 eV to ionization events occurring from π-orbitals.

The starting point of our interpretation, therefore, is the π-system of a regular ring. Using a simple HMO model that takes into account first-order bond fixation[5] we calculate four bands below 11.5 eV for the planar [10]annulene (**2**), two at 7.9 eV and two at 11.1 and 11.2 eV due to ionizations from the MOs e_{2u} and e_{1g}.

Owing to the reduction of the symmetry of (**1**) from D_{10h} to (at least) C_s we expect a resulting split of the energy levels. Furthermore, the non-planarity of (**1**) together with the central CMe moiety will favour π–σ interaction, which should influence the lower π-levels considerably. This explains qualitatively the discrepancy between the results of our simple HMO model (see Table) and the experimental results.

To gain support for our assignment we have carried out MINDO/3 calculations[6] on (**1**). Imposing no symmetry restriction, the calculation predicts that bond alternation around the perimeter should be preferred. The energy difference between (**1**) with C_s symmetry and (**1**) with C_1 symmetry amounts to 5 kcal mol^{-1}. The predicted C–C bond lengths are given in Figure 2(*a*). The results are in good agreement with those obtained by MNDO SCF-MO calculations.[7] The calculated orbital energies are listed in the Table. A comparison with the experimental ionization energies shows a close agreement between experiment and calculation in the case of the first two values, corresponding to $17a'$ and $12a''$ of (**1**) (assuming C_s symmetry) shown in Figure 2(*b*). The separation between $16a'$ and $11a''$ is predicted to be 0.3 eV and suggests the assignment of bands 3 and 4 of the p.e. spectrum to these two values. The numerical agreement between $16a'$ and $11a''$ and the experiment is, however, less satisfactory compared with bands 1 and 2. We presume that this discrepancy is caused by a shortcoming of MINDO/3, placing the σ-orbitals at too low an energy.

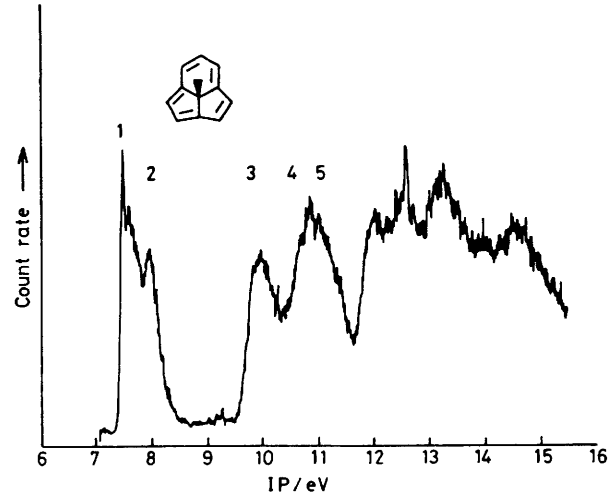


Figure 1. He^{I} photoelectron spectrum of compound (**1**)

Our assignment of band 3 to only one transition ($11a''$) must be a tentative one since we cannot rule out the alternative of assigning two transitions ($11a''$ and $16a'$) to it. Neither of the methods of calculation applied nor the comparison of the areas of bands yields a definite answer. A solution to this problem might be obtained by studying derivatives of (**1**).

Concluding Remarks

The highest occupied π-orbitals of (**1**), as well as those of 1,6-methano[10]annulene (**3**), can be derived from those of a regular [10]annulene (**2**) using first-order perturbation theory. Compounds (**1**) and (**3**) differ with respect to their transannular interactions, the alkyl groups (CH_2 *versus* CMe), and their planarity.

X-Ray investigations on (**3**) reveal a distance of 2.4 Å between centres 1 and 6. Our calculations predict a larger distance between atoms 4a and 7a but a similar separation between 2a and 4a or 7a in compound (**1**) (Figure 2).

A comparison between the two molecules shows much less coplanarity of the [10]ring in (**3**) compared with (**1**). Consequently, we expect a stronger π–σ interaction in (**3**) than in (**1**). This should show up especially in the lower π-MOs. In our correlation diagram (Figure 3) between an unperturbed planar [10]annulene (**2**) we have considered this latter difference by assuming different basis orbital energies for e_{1g} of the [10]annulene.

Table. Comparison between the recorded vertical ionization energies, $I_{v,j}$, and the calculated orbital energies, ε_j, of compounds (**1**) and (**2**). All values in eV

Band	$I_{v,j}$	Assignment[a]	$-\varepsilon_j$(1)(MINDO/3)	$-\varepsilon_j$(2)(HMO)
1	7.56 7.66	$17a'(\pi)$	7.80	7.88
2	8.05	$12a''(\pi)$	8.02	7.88
3	10.0	$11a''(\pi)$	9.24	11.1
4	10.7	$16a'(\pi)$	9.53	11.2
5	11.0	$15a'$		

[a] The numbers refer to the valence electrons only.

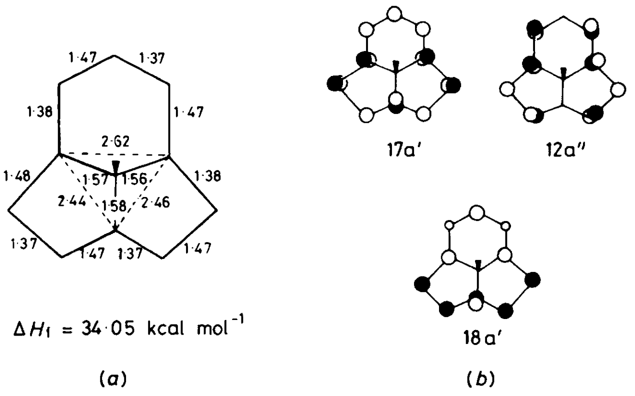


Figure 2. (*a*) Calculated bond lengths of (**1**) according to MINDO/3. (*b*) Schematic drawing of the highest occupied ($17a'$ and $12a''$) and lowest unoccupied ($18a'$) MOs of (**1**)

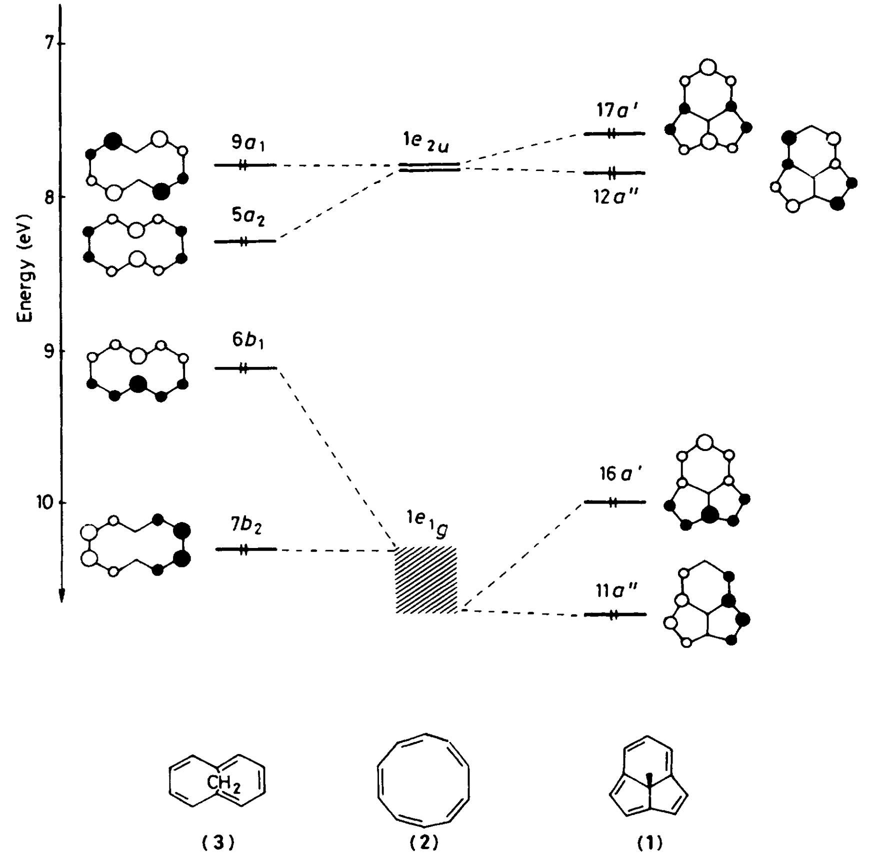
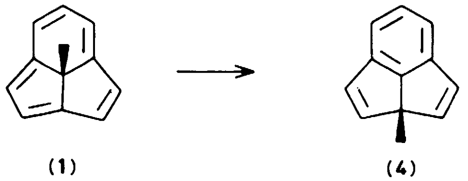


Figure 3. Comparison between the first bands of the p.e. spectra of (**1**) (right) and (**3**) (left) with the calculated levels of an unperturbed plana [10]annulene (**2**). For the different basis energies of the $1e_{1g}$ level see text. The numbers refer to the valence electrons only



(1) (4)

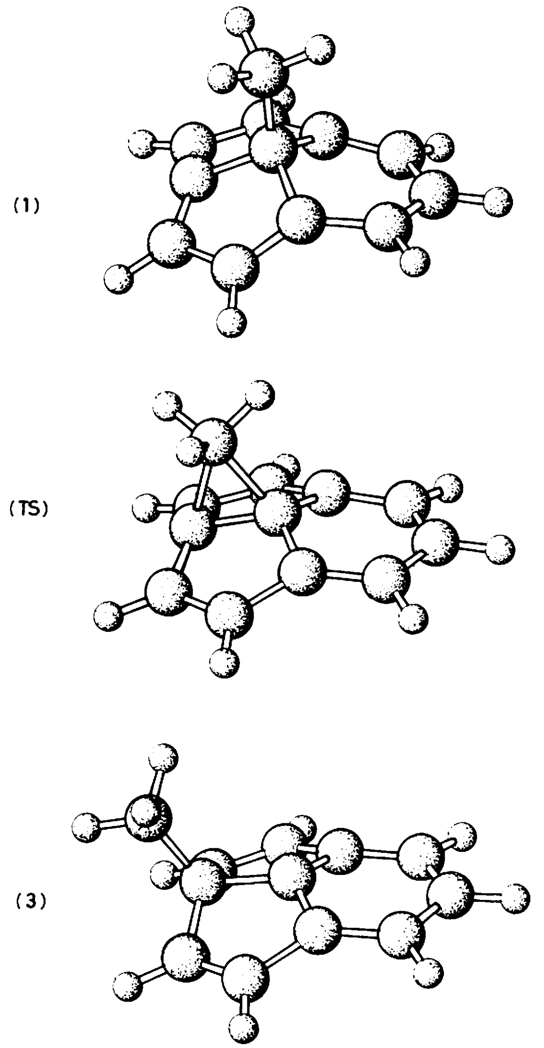


Figure 4. Comparison of the calculated geometries of (**1**), (**4**), and the transition state (**TS**) for the rearrangement of (**1**) to (**4**)

Strong transannular interactions yield a stabilization (5a_2) and destabilization (6b_1) in the case of (**3**).[4] For (**1**) transannular interactions between centre 2a and 4a as well as 7a lead to a destabilization of 17a' and 16a' with respect to the basis of an inductively perturbed [10]annulene.

In view of reactions that will be carried out on (**1**) we have drawn the two highest occupied MOs (17a' and 12a'') and the lowest unoccupied MO of (**1**) (18a') in Figure 2(*b*). In the case of the HOMOs we encounter a similar tilting of the $2p_\pi$-lobes as in (**3**).[8]

A further reaction of interest is the thermal rearrangement of (**1**) to the 2a*H*-isomer (**4**).[4] Based on kinetic studies[1] this reaction has been interpreted as an unimolecular [1,5]sigmatropic shift of the methyl group. The activation energy of this process was found to be 32.7 kcal mol^{-1}. An MINDO/3 calculation yields a value of 37.3 kcal mol^{-1} and an energy difference of 12.9 kcal mol^{-1} between (**1**) and (**4**), the latter being the more stable. In Figure 4 we show the geometries of (**1**), (**4**), and the transition state (**TS**) as derived by the MINDO/3 calculation. It is seen that the system is almost flat in the transition state and the methyl group is bridging the centres 7b and 2a. The stabilizing effect of the benzene ring that is formed in the transition state is estimated to be 15 kcal mol^{-1}. This follows from the comparison of the above result with that reached by calculating the corresponding 1,5-methyl shift in monomethylcyclopentadiene, for which a corresponding activation barrier of 47.6 kcal mol^{-1} has been predicted by MINDO/3. This value compares well with the results found for the 1,5-methyl shift in di- and tri-methylcyclopentadienes.[9]

Experimental

The preparation of (**1**) has been described.[1] The He^{I} spectrum of the analytically pure compound was recorded on a Leybold-Heraeus UPG 200 spectrometer at room temperature. The spectrum has been calibrated with Ar and Xe, a resolution of 25 meV of the $^2p_{3/2}$ Ar line was obtained.

Acknowledgements

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References

1 T. L. Gilchrist, D. Tuddenham, R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1981, 657; Z. Lidert and C. W. Rees, *ibid.*, 1982, 499; R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1984, 165.
2 T. Koopmans, *Physica, Utrecht*, 1934, **1**, 104.
3 R. Gleiter and P. Bischof, 'Topics in Nonbenzenoid Aromatic Chemistry,' Hirokawa Publish. Co., Tokyo, 1977, vol. 1, p. 1; P. Bischof, R. Gleiter, K. Hafner, M. Kobayashi, and J. Spanget-Larsen, *Ber. Bunsenges., Phys. Chem.*, 1976, **80**, 532; R. Gleiter, J. Spanget-Larsen, E. W. Thulstrup, I. Murata, K. Nakasuji, and C. Jutz, *Helv. Chim. Acta*, 1976, **59**, 1459; P. Bischof, R. Gleiter, K. Hafner, K.-H. Knauer, J. Spanget-Larsen, and H. U. Süss, *Chem. Ber.*, 1978, **111**, 932.
4 R. Boschi, W. Schmidt, and J.-C. Gfeller, *Tetrahedron Lett.*, 1972, 4107; C. Batich, E. Heilbronner, and E. Vogel, *Helv. Chim. Acta*, 1974, **57**, 2288; R. R. Andréa, H. Cerfontein, H. J. A. Lambrechts, I. N. Louwen, and A. Oskam, *J. Am. Chem. Soc.*, 1984, **106**, 2531.
5 F. Brogli and E. Heilbronner, *Theor. Chim. Acta*, 1972, **26**, 289.
6 R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285; P. Bischof, *ibid.*, 1976, **98**, 6844.
7 H. S. Rzepa, *J. Chem. Res.* (*M*), 1982, 3301.
8 R. Gleiter, M. C. Böhm, and E. Vogel, *Angew. Chem.*, 1982, **94**, 925; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 922.
9 C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.

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