Orbital Interactions in "Hypostrophene" and its Hydro- and Homo-Derivatives.
A Photoelectron Spectroscopic Investigation

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Analysis of the first bands in the He(I) photoelectron spectra of "hypostrophene" (tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-diene, **3**), its tetrahydro- (**1**), dihydro- (**2**), homo- (**4**), and bishomo-derivative (**5**) has been achieved on the basis of the correlations within the series **1** to **5** with accompanying semiempirical calculations of the MINDO/3 and SPINDO/1 type. The electronic structure of the first excited states of **3** and *syn*-tricyclo[4.2.0.0^{2,5}]octadiene is discussed in light of their inability to undergo [π^2s + π^2s] ring closure.

Orbital-Wechselwirkungen in „Hypostrophen", seinen Hydro- und Homo-Derivaten.
Eine photoelektronenspektroskopische Untersuchung

Die Analyse der ersten Banden in den He(I)-Photoelektronen(PE)-Spektren von „Hypostrophen" (Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-dien, **3**) sowie seiner Tetrahydro- (**1**), Dihydro- (**2**), Homo- (**4**) und Bishomo-Derivate (**5**) beruht auf der Korrelation zwischen den Spektren von **1** bis **5** sowie dem Vergleich mit den Ergebnissen von semiempirischen Rechnungen vom MINDO/3 und SPINDO/1-Typ. Die Elektronenstruktur des ersten angeregten Zustands von **3** und *syn*-Tricyclo[4.2.0.0^{2,5}]octadien wird im Zusammenhang mit dem Ausbleiben einer [π^2s + π^2s]-Reaktion diskutiert.

Soon after the first synthesis of the interesting hydrocarbon "hypostrophene" (tetra-cyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-diene, **3**)[1], an investigation of its He(I) photo-electron(PE) spectrum was carried out[2]. The results of semiempirical calculations suggested that the first band is attributable to ionization from the symmetrical linear combination of the π orbitals as a direct consequence of strong σ-π interaction. The assignment of all other bands was uncertain.

To gain further insight into the electronic structure of this highly strained fused-ring system, we have presently extended this investigation to the tetrahydro- (**1**), dihydro- (**2**), homo- (**4**), and bishomo- (**5**) derivatives. Our assignments of the PE bands

of these derivatives are based upon systematic correlation of levels within the series which includes **3** and on the results of MINDO/3[3,4] and SPINDO/1[5,6] molecular orbital (MO) calculations which presuppose the validity of Koopmans' theorem (ε_{MO} = $-I_v$)[7]. The resulting analysis of the electronic structure of "hypostrophene" (**3**) differs substantially from that obtained in the first investigation[2].

Preparation, PE-Spectra, and Calculational Procedures

The synthesis of hydrocarbons **4** and **5** has been previously described[8a]. Access to **1** and **2** was achieved by suitably controlled diimide reduction of **3**[8b].
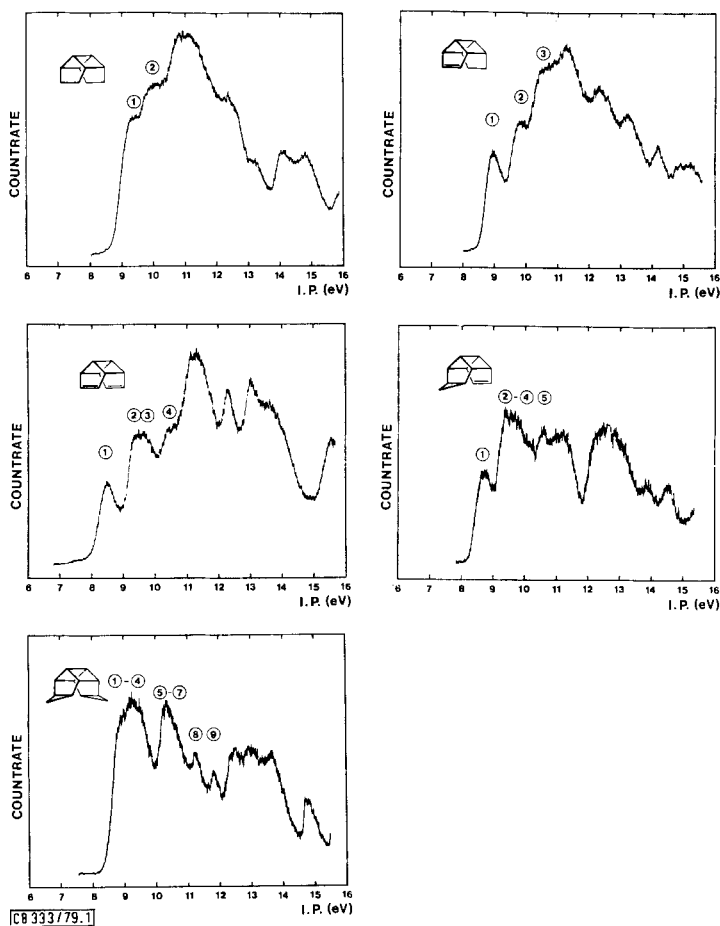

Figure 1. PE spectra of **1** to **5**

The PE spectrum of **3** has been published previously[2], but as no ionization energies were reported we have remeasured the spectrum. The PE spectra of **1** – **5** shown in Figure 1 were recorded at room temperature on a PS 18 instrument (Perkin Elmer Ltd.,

England) with a He(I) light source. The spectra were calibrated with argon; a resolution of about 20 meV on the argon line was obtained.

Calculations dealing with structures **1 – 5** were carried out by approximate semi-empirical valence electron methods of the MINDO/3[3,4] and SPINDO/1[5,6] type. The molecular geometries were taken as those predicted by MINDO/3; C_{2v} symmetry was assumed for **1**, **3** and **5** and C_s symmetry for the remaining compounds.

Results and Discussion

The measured vertical ionization energies $(I_{v,J})$ and calculated MO energies (ε_J) are given in the Table, while the correlation of levels in the series **1 – 5** is provided in Figure 2.

Table. Measured vertical ionization energies $I_{v,J}$ and calculated orbital energies ε_J (eV). The numbering of the symmetry labels refers to valence orbitals only

Compound	Band	$I_{v,J}$	Orbital assignment	ε_J(MINDO/3)	ε_J(SPINDO/1)
1 (C_{2v})	①	9.4	$5\,a_2(\sigma)$	$-9.20(5\,a_2)$	$-10.81(5\,a_2)$
	②	≈ 10.0		$-9.72(9\,a_1)$	$-11.42(6\,b_2)$
				$-10.11(7\,b_1)$	$-11.54(9\,a_1)$
				$-10.18(6\,b_2)$	$-11.74(7\,b_1)$
2 (C_s)	①	8.7_2	$16\,a'(\pi)$	$-9.14(16\,a')$	$-9.99(16\,a')$
	②	9.6	$10\,a''(\sigma)$	$-9.14(10\,a'')$	$-10.61(10\,a'')$
	③	≈ 10.3		$-9.79(15\,a')$	$-11.42(15\,a')$
				$-10.17(14\,a')$	$-11.45(9\,a'')$
3 (C_{2v})	①	8.4_4	$9\,a_1(\pi_+)$	$-8.62(9\,a_1)$	$-9.51(9\,a_1)$
	②	9.4	$7\,b_1(\pi_-)$	$-9.17(4\,a_2)$	$-10.20(7\,b_1)$
	③	9.7	$4\,a_2(\sigma)$	$-9.57(7\,b_1)$	$-10.52(4\,a_2)$
	④	≈ 10.4		$-9.81(8\,a_1)$	$-11.30(8\,a_1)$
				$-10.53(6\,b_1)$	$-11.66(6\,b_1)$
4 (C_s)	①	8.7	$18\,a'(\pi)$	$-8.95(18\,a')$	$-10.00(18\,a')$
	②	9.4	$17\,a'(w_S)$	$-9.10(10\,a'')$	$-10.29(17\,a')$
	③	≈ 9.7	$10\,a''(\sigma)$	$-9.39(17\,a')$	$-10.58(10\,a'')$
	④	≈ 10.2	$9\,a''(w_A)$	$-9.86(9\,a'')$	$-11.05(9\,a'')$
	⑤	10.6		$-9.86(16\,a')$	$-11.35(16\,a')$
5 (C_{2v})	①⎫		⎧$11\,a_1(w_S^+)$	$-9.11(11\,a_1)$	$-10.32(9\,b_1)$
	②⎪	$9.0-9.8$	⎪$9\,b_1(w_S^-)$	$-9.17(5\,a_2)$	$-10.51(11\,a_1)$
	③⎬		⎨$5\,a_2(\sigma)$	$-9.29(9\,b_1)$	$-10.82(5\,a_2)$
	④⎭		⎩$6\,b_2(w_A^+)$	$-9.55(6\,b_2)$	$-10.96(6\,b_2)$
	⑤⎫		⎧$4\,a_2(w_A^-)$	$-9.86(8\,b_1)$	$-11.47(4\,a_2)$
	⑥⎬	$10.4-10.9$	⎨$8\,b_1(\sigma)$	$-9.95(10\,a_1)$	$-11.48(8\,b_1)$
	⑦⎭		⎩$10\,a_1(\sigma)$	$-10.45(4\,a_2)$	$-11.49(10\,a_1)$
	⑧	11.4		$-10.77(3\,a_2)$	$-12.14(3\,a_2)$
	⑨	12.0		$-11.45(9\,a_1)$	$-12.49(9\,a_1)$

It is evident that the binding energies predicted by SPINDO/1 are too high by about 1 eV. This may be due to the use of estimated geometries; however, a similar discrepancy was found in the case of norbornadiene despite use of the experimental geometry[6]. In contrast, the MINDO/3 results appear in better numerical agreement with the PE data, at least as far as the first few levels are concerned. The consistency is particularly strik-ing when the general tendency of this method to intermingle σ- and π-levels is tenta-
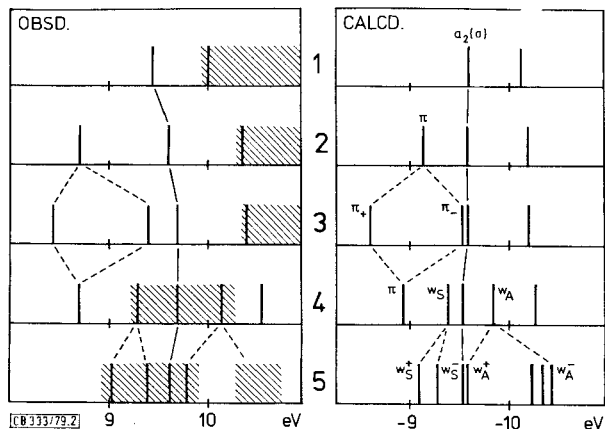
Figure 2. (Right) Correlation of calculated MINDO/3 MO energies. The σ levels are shifted by 0.4 eV towards higher binding energy.
(Left) Correlation of observed PE bands according to the suggested assignment

tively corrected for (Figure 2). The present situation closely parallels that encountered in our previous investigation of tricyclooctadienes and their homo derivatives[9].

Both methods predict the highest occupied MO (HOMO) of **1** to be $5a_2$. This MO is highly localized in the bicyclohexane fragment and closely related to the $3a_2$ HOMO of bicyclo[2.2.0]hexane (**6**)[10].
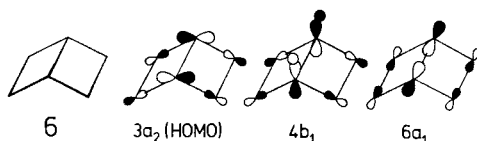
The first PE band of **1** at 9.4 eV must be assigned to ejection of an electron from this orbital. The corresponding band of **6** is seen at 9.6 eV[10], an observation which is consistent with a shift caused by the inductive effects of the additional alkyl moieties in **1**. This assignment is at variance with the one suggested previously[2], insofar as the HOMO of **6** was considered to be the $6a_1$ orbital for which an effective binding energy of 10.5 eV was estimated. According to the earlier analysis of the PE spectrum of **6**[10], however, the latter orbital is responsible for the third band (measured at 10.8 eV), the first and the second (9.6 and 10.2 eV) being assigned to $3a_2$ and $4b_1$, respectively.

For reasons of symmetry, the orbital corresponding to the HOMO of **1** ($5a_2$) is unable to interact with any of the π-type orbitals in **2** and **3**. Furthermore, as this orbital is localized almost entirely in the bicyclohexane moiety, one would expect its energy to remain relatively unaffected while transforming **1** to **2** and **2** to **3**. This expectation is confirmed by the calculational results, particularly those obtained by MINDO/3 (Figure 2). The peaks at 9.6 and 9.7 eV in the PE spectra of **2** and **3** are therefore assigned to this level which is indicated as "σ" in the Table. This assignment implies a small but significant shift towards higher binding energies through the series **1** → **2** → **3**, a conclu-

sion consistent with general experiences concerning the shift of the onset of σ-bands on successive introduction of unsaturation into a saturated hydrocarbon. In the case of **3**, this causes us to prefer assignment of the peak at 9.7 eV rather than that at 9.4 eV to this orbital; selection of the latter would lead to a reversal of the above mentioned trend. *Schmidt* and *Wilkins*[2] assigned the peak at 9.7 eV to the $8a_1$ orbital, corresponding to the $6a_1$ bicyclohexane orbital which they considered to be the HOMO of **6**. It is our belief that the shoulder at 10.4 eV may be assigned to this level, as suggested by the results of the calculations.

The π-band of **2** is observed at 8.7 eV, about 0.5 eV lower than that of reference compounds such as dimethylethylene[11] and cyclopentene[12]. The calculated MO's indicate that the shift towards lower binding energies is largely due to conjugative interaction of the ethylenic π orbital with high-lying orbitals of the bicyclohexane moiety, particularly the $4b_1$ orbital discussed above. The π orbital character of the resulting MO, $16a'$ (π), is predicted to be 60% by MINDO/3 and 80% by SPINDO/1.

In the case of **3**, the PE peaks at 8.4 and 9.4 eV are attributed to ejection of electrons from orbitals of predominantly π character, $9a_1(\pi_+)$ and $7b_1(\pi_-)$, respectively. This assignment is consistent with our calculations and in agreement with the conclusions of *Schmidt* and *Wilkins*[2]. Again, considerable interaction with bicyclohexane orbitals is predicted. The in-phase combination of the two ethylenic π orbitals, π_+, mixes strongly with several totally symmetric bicyclohexane orbitals, such as the $6a_1$ indicated above. Inspection of the calculated wavefunctions indicates that although $6a_1$ is closest in energy, it is not the dominant admixture. Rather, several orbitals contribute to comparable degrees. The situation appears to be less complicated in the case of the out-of-phase combination π_-, which interacts predominantly with the $4b_1$ bicyclohexane orbital.

The approximate shape of the resulting π-type MO's of **3** is indicated below (the plane of the paper is perpendicular to the double bonds). Note that $9a_1(\pi_+)$ has insignificant amplitude on the bicyclohexane bridgehead atoms, in contrast to the $6a_1$ orbital of **6** (see above), indicating that the latter is not a dominant admixture. The pure π orbital characters calculated by MINDO/3 (SPINDO/1) is 54% (70%) for $9a_1$ and 65% (93%) for $7b_1$. The SPINDO/1 results are probably the more realistic, owing to the tendency of MINDO/3 to place σ levels at too low binding energies relative to π levels.

$9a_1 (\pi_+)$ $7b_1 (\pi_-)$
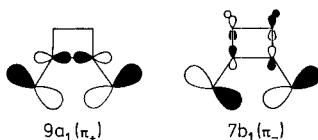
The type of interaction discussed above is usually referred to as "through-bond" coupling, as opposed to "through-space" interaction which stabilizes π_+ and destabilizes π_- because of direct overlap of the ethylenic π orbitals in **3**. In the present case, "through-bond" effects dominate so that $9a_1(\pi_+)$ appears on top of $7b_1(\pi_-)$. According to the analysis by *Schmidt* and *Wilkins*[2], this ordering is the result of strong "through-bond" coupling via "an exceptionally high-lying σ level", *i. e.*, the bicyclohexane $6a_1$ level. However, in the first place, the $6a_1$ level is not exceptionally high-lying – it corresponds to the third highest occupied MO of **6**[10]. Secondly, as pointed out above, the "through-bond" mechanism leading to the strong destabilization of π_+ is

probably quite complicated, involving the bicyclohexane $6a_1$ orbital to only a minor degree.

The first band in the PE spectrum of the homo-derivative **4** has a maximum at 8.7 eV. We assign this band to the π-type orbital, $18a'$ (π), in agreement with the calculational results. The ensuing region of the spectrum is complicated and contains several overlapping bands. The computations predict that the highest σ-level of **3** ($4a_2$) is insignificantly affected by replacement of a double bond with a cyclopropane ring. This fact indicates to us that the corresponding ionization event in the case of **4** occurs close to 9.7 eV. The cyclopropane Walsh-type[13] orbitals, w_S and w_A, are also expected to give rise to PE bands in this region. We tentatively assign the PE features close to 9.4 and 10.2 eV to ionizations from $17a'$ (w_S) and $9a''$ (w_A), respectively. The prediction that $17a'$ (w_S) has lower binding energy than $9a''$ (w_A) is consistent with the higher amplitude of w_S on the substituted centers.

The bishomo derivative **5** is an interesting compound, due to its unique topology of fused 3-, 4-, and 5-membered rings. Unfortunately, the low energy region of the PE spectrum is too complex to allow a detailed analysis. Two broad bands are found in the regions $9.0 - 9.8$ eV and $10.4 - 10.9$ eV, followed by sharper peaks at 11.4 and 12.0 eV. The computational results indicate that the first broad band is due to four and the second to three independent ionization processes, as indicated in Figure 2 and the Table. A rather large gap is predicted between the MO's derived from the in-phase and out-of-phase combinations of the w_A Walsh-type orbitals, $6b_2(w_A^+)$ and $4a_2(w_A^-)$, respectively. This is due to strong interaction of the cyclopropane w_A^+ combination with a lower lying bicyclohexane orbital which corresponds to the fifth highest occupied MO of **6** ($4b_2$)[10]. In the case of w_A^-, "through-bond" effects play only a minor role.

$6b_2(w_A^+)$

Concluding Remarks

The inability of "hypostrophene" (**3**) to undergo a light induced $[\pi^2s + \pi^2s]$ intramolecular cycloaddition reaction leading to pentaprismane has been ascribed as a consequence of the presence of π_+ as HOMO and π_-^* as LUMO[2]. The conclusion that π_+ is the HOMO is confirmed by our study. However, the two lowest unoccupied MO's, π_-^* and π_+^*, are predicted to be essentially near-degenerate, which complicates the application of simple symmetry rules. A similar situation applies to syn-tricyclo[4.2.0.0²,⁵]octadiene which exhibits analogous spectroscopic[8,14] and chemical behavior[15]. An attempt to investigate the excited states of these compounds by means of CNDO-CI calculations has led to ambiguous results, largely because of the extreme sensitivity of the calculational results to variations of molecular geometry.

It is thus possible that steric and electronic constraints may "allow" derivatives of **3** or syn-tricyclo[4.2.0.0²,⁵]octadiene to follow a $[\pi^2s + \pi^2s]$ reaction path. The interesting phototetramerization of tolane to octaphenylcubane[16] may prove to be such a case.

Experimental Part

Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]decan (Tetrahydrohypostrophene, **1**): A solution containing 0.10 g of hypostrophene (**3**) in 25 ml of methanol was cooled to 0 °C under nitrogen and treated with 2.0 g of dipotassium azodicarboxylate and 2.6 ml of acetic acid during 15 min. After 3 h, the pre-described workup was employed. Removal of solvent left 60 mg of **1**. — ^{1}H NMR (CDCl$_3$): δ = 2.88 (m, 6 H) and 2.00 – 1.20 (m, 8 H); ^{13}C NMR (CDCl$_3$): δ = 43.43 (2 C), 40.41 (4 C), and 27.84 (4 C).

C$_{10}$H$_{14}$ (134.1)   Calcd. C 89.49 H 10.51   Found C 89.49 H 10.35

Tetracyclo[5.3.0.0^{2,6},0^{3,10}]dec-4-en (Dihydrohypostrophene, **2**): Potassium azodicarboxylate (117 mg, 0.6 mmol) was added in one portion to a stirred, cooled (0 °C) solution of hypostrophene (52 mg, 0.4 mmol) in 3 ml absolute methanol under an argon atmosphere. Glacial acetic acid (0.11 ml) was introduced and stirring was maintained at 0 °C until the yellow color faded. The excess acetic acid was neutralized by addition of sodium hydrogencarbonate and the resultant mixture was diluted with 35 – 40 ml of water and extracted three times with ether. The combined ethereal extracts were washed with saturated sodium hydrogencarbonate solution and water before drying. Filtration and careful solvent removal under vacuum at room temperature gave a low melting semi-solid which consisted of unreacted hypostrophene as well as dihydro and tetra-hydro derivatives.

Preparative vpc (12 ft 10% PMPE 6-ring, 110 °C) gave dihydrohypostrophene (8.1 mg) as a clear colorless solid. ^{1}H NMR (100 MHz, CDCl$_3$): δ = 6.28 (s, 2 H), 3.55 – 2.69 (m, 6 H) and 1.59 (s, 4 H); *m/e* calcd. 132.0939, obs. 132.0943.

References

[1] *J. S. McKennies, L. Brenner, J. S. Ward,* and *R. Pettit,* J. Am. Chem. Soc. **93**, 4957 (1971).
[2] *W. Schmidt* and *B. T. Wilkins,* Tetrahedron **28**, 5649 (1972).
[3] *R. C. Bingham, M. J. S. Dewar,* and *D. H. Lo,* J. Am. Chem. Soc. **97**, 1285 (1975), and subse-quent papers.
[4] *P. Bischof,* J. Am. Chem. Soc. **98**, 6844 (1976).
[5] *L. Asbrink, C. Fridh,* and *E. Lindholm,* J. Am. Chem. Soc. **94**, 5501 (1972); *C. Fridh, L. Asbrink,* and *E. Lindholm,* Chem. Phys. Lett. **15**, 282 (1972).
[6] *E. Lindholm, C. Fridh,* and *L. Asbrink,* Discuss. Faraday Soc. **54**, 127 (1972).
[7] *T. Koopmans,* Physica **1**, 104 (1934).
[8] [8a] *L. A. Paquette, D. R. James,* and *G. Klein,* J. Org. Chem. **43**, 1287 (1978). — [8b] *L. A. Pa-quette, R. F. Davis,* and *D. R. James,* Tetrahedron Lett. **1974**, 1615.
[9] *J. Spanget-Larsen, R. Gleiter, L. A. Paquette, M. J. Carmody,* and *C. R. Degenhardt,* Theor. Chim. Acta **50**, 145 (1978).
[10] *G. Bieri, E. Heilbronner, T. Kobayashi, A. Schmelzer, M. J. Goldstein, R. J. Leight,* and *M. S. Lipton,* Helv. Chim. Acta **59**, 2657 (1976).
[11] *E. Haselbach, J. A. Hashmall, E. Heilbronner,* and *V. Hornung,* Angew. Chem. **81**, 897 (1969); Angew. Chem., Int. Ed. Engl. **8**, 878 (1969).
[12] *P. Bischof* and *E. Heilbronner,* Helv. Chim. Acta **53**, 1677 (1970).
[13] *A. D. Walsh,* Nature (London) **159**, 167 (1947); **159**, 712 (1947); *T. M. Sudgen,* ibid. **160**, 367 (1947); *A. D. Walsh,* Trans. Faraday Soc. **45**, 179 (1949).
[14] *R. Gleiter, E. Heilbronner, M. Hekman,* and *H.-D. Martin,* Chem. Ber. **106**, 28 (1973).
[15] Irradiation of *syn*-octamethyltricyclo[4.2.0.0^{2,5}]octadiene did not give the corresponding cubane: *R. Criegee,* Angew. Chem. **74**, 703 (1962); Angew. Chem., Int. Ed. Engl. **1**, 519 (1962).
[16] *G. Büchi, G. W. Peny,* and *E. W. Robb,* J. Org. Chem. **27**, 4107 (1962); *J. M. Slobodin* and *A. P. Chitrov,* J. Org. Chem. USSR **6**, 1756 (1970).

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