Small and Medium Rings, 77[1]

Nonconjugated π,π Interactions Approaching Classical π,π Conjugation – PE-Spectroscopical Investigation of the 7,8;12,19-Diseco-1,16-dodecahedradiene System

Dominik Elsässer[a], **Karin Hassenrück**[a], **Hans-Dieter Martin***[a], **Bernhard Mayer**[a], **Georg Lutz**[b], **Horst Prinzbach***[b]

Institut für Organische Chemie und Makromolekulare Chemie der Universität Düsseldorf[a],
Universitätsstr. 1, W-4000 Düsseldorf 1, F.R.G.

Chemisches Laboratorium der Universität Freiburg i. Br., Institut für Organische Chemie und Biochemie[b],
Albertstr. 21, W-7800 Freiburg i. Br., F.R.G.

Received July 3, 1991

Key Words: Disecododecahedradienes / Pagodanes / PE spectroscopy / π-Orbital interaction / Orbitals, localized, precanonical / Orbital interaction, through-space

---

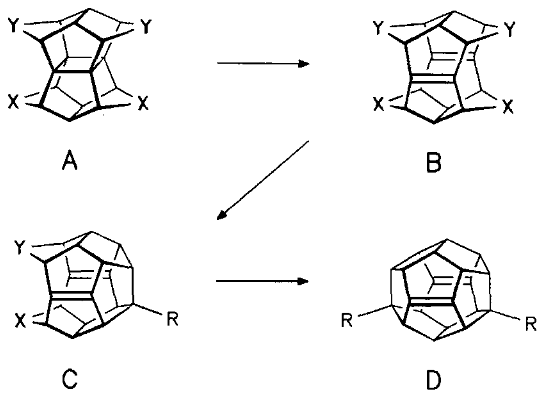
Transannular (orbital) interactions in compounds **1**–**9** are studied by means of He(I_α)-PE spectroscopy. Unusually strong through-space-dominated π,π interaction is found to be operative in the nonconjugated 1,6-dienes **1**, **2**, **7**, and **8**. The π,π splitting of 1.9 eV for disecododecahedradiene **1** is even surpassed by the record value of 2.2 eV for disecodienedione **2**, which almost equals that in 1,3-butadiene (2.46 eV). The experimental results are explained by computational methods, especially by analyses of the precanonical MOs.

Homoconjugation[2] – electronic interaction between systems not directly linked to each other and operating through space (OITS) as well as through bonds (OITB) – is a much proven, chemically relevant phenomenon[3]. Specifically, orbital interaction through space has been extensively studied for various subsystems under the aspects of proximity, angular relationship, orbital energies. Yet, excitement beyond routine arises, whenever "extremes" are involved. Examples of this latter sort, bringing homoconjugation very close to classical conjugation, are the subject of this paper.

7,8;12,19-Diseco-1,16-dodecahedradienes ("pagodadienes") **B** (X, Y = CR_2) are pivotal intermediates in the synthetic sequence from pagodanes **A** to dodecahedradienes **D**. It is only after opening of the four-membered ring in **A**, that opposite X,Y-positions are close enough to allow installation of the lateral bonds[4,5]. By making recourse to S_N2-type[6] methodologies, ring closures **B**→**C** and **C**→**D** have been brought about in appropriately functionalized derivatives. Functional-group eliminations lead subsequently to the parent, 1,16-dodecahedradiene (**D**, R = H) and are being pursued for the parent secodiene **C** (X = Y = CH_2, R = H). The special nature of the skeletons **B** and **D** guarantees the perfect synperiplanar arrangement of the two bridged π bonds and also a surprisingly high kinetic stability of the increasingly strained compounds.

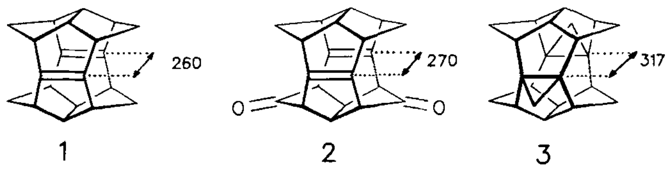
The variation in transannular interaction with changing geometry (varying X,Y-chain lengths) and the chemical consequences are one of the fascinating topics emanating from these novel molecular skeletons. In this paper we will deal with dienes of type **B**.

Scheme 1



In disecododecahedradiene **1** (dienedione **2**) the π,π distance (C1–C12) is calculated (MM2) to be only 262 pm (270 pm), what is probably only slightly too short[7]. In a recent comparison of the calculated and experimental structure of a secodiene **C** a rather good agreement for the transannular distances has been observed[8].

Scheme 2

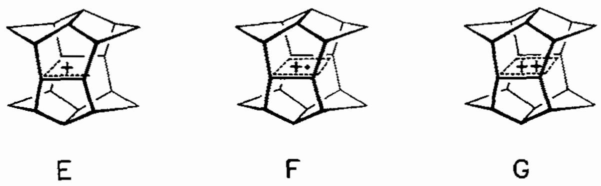


Distances in pm.

Chem. Ber. **124** (1991) 2863–2869 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1991 0009–2940/91/1212–2863 $ 3.50+.25/0

There are indeed strong qualitative manifestations for π,π interaction and π,π repulsion in neutral dienes **B**, e. g. long-wavelength UV absorption, transannular additions, compensation for olefinic hyperstability. Strong transannular bonding effects have been noted for charged species of this sort – in cations **E**[9], radical cations **F**[10] and, above all, in σ-bishomoaromatic dications **G**[11].

Scheme 3



Given the unusually favorable topology for π,π homoconjugation in the disecododecahedradiene skeletons, it was tempting to look once more (cf. i.a. **10**)[12,13] for direct σ,σ homoconjugative interaction in the biscyclopropanated derivative **3**. An X-ray analysis[14] has confirmed the perfect synperiplanar orientation of the cyclopropane rings, and thus of the relevant Walsh orbitals; yet, the C1 – C12 distance of 317 pm (327 pm, MM2) is rather large[15,16].

Quantification of OITS effects in substrates **1**, **2**, and **3** is being pursued, in continuation of our longstanding interests in multichromophoric systems[3,17], by He(I_α)-PE spectros-

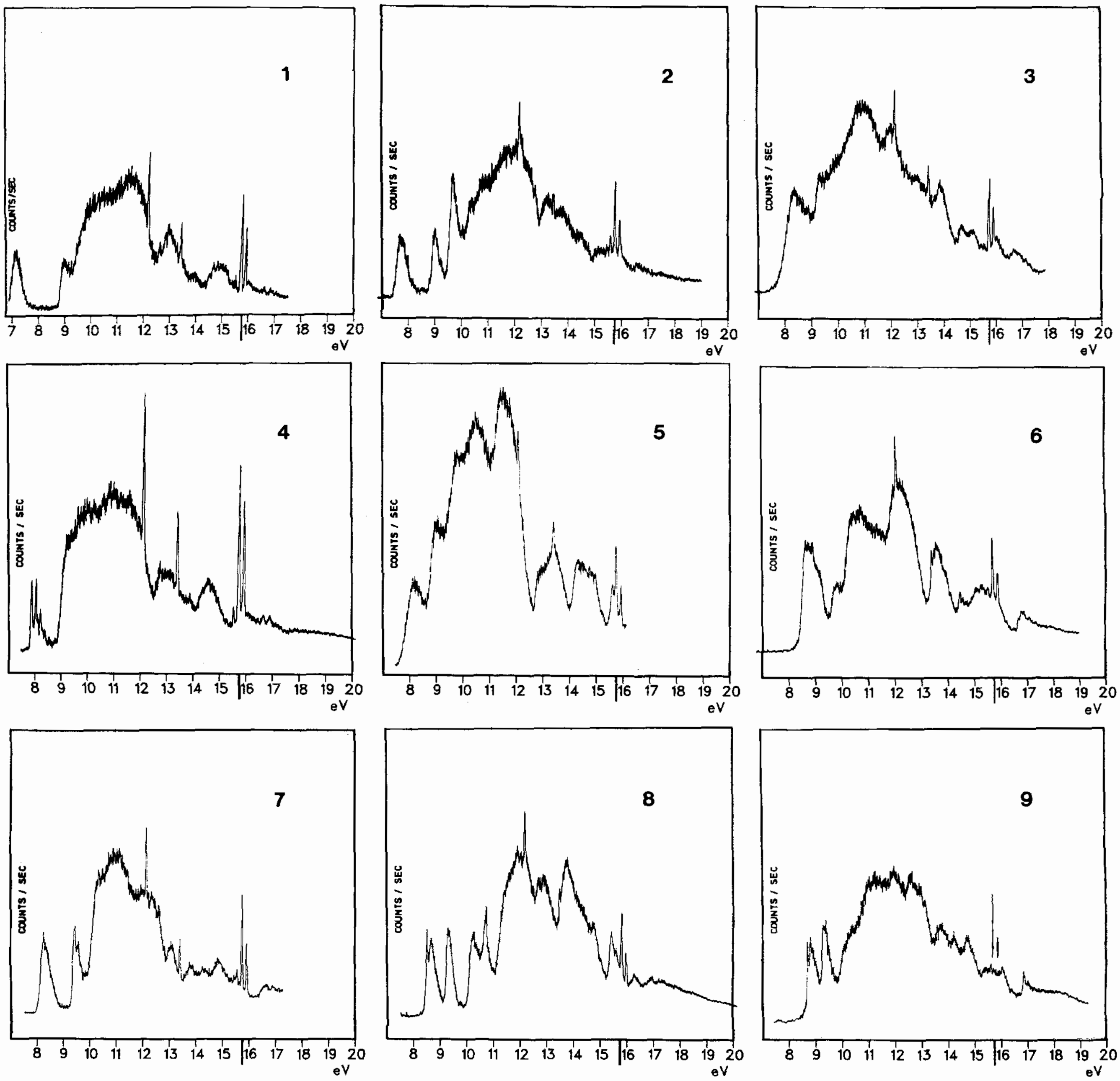
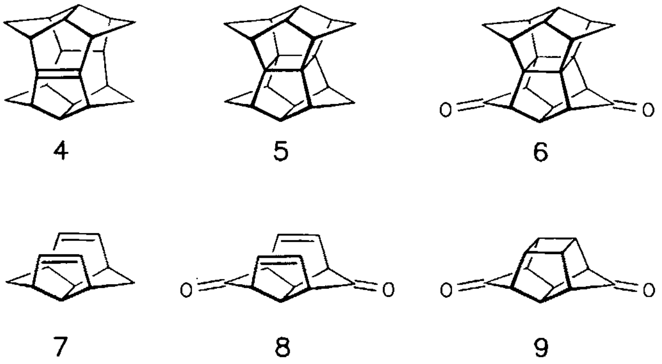


Figure 1. He(I_α)-PE spectra of **1** – **9**

copy. The measured energy difference between neutral ground state and radical cation is, by making use of Koopmans' theorem[18], related to the respective π orbitals. In addition, various computational methods are applied in the interpretation of the experimental spectra. Included in this study are the disecoene **4**[7], the parent pagodane **5**[19], its dione **6**[20], and the molecular "halves" **7**–**9**[21] as model systems. Like **1**–**3**, all these compounds are sufficiently stable to allow vaporization without any decomposition.

Scheme 4



PE Spectroscopy[22]

The PE spectra of **1**–**9** are shown in Figure 1, the relevant band energies are graphically correlated in Figure 2. In Table 1 results from semiempirical and ab initio calculations are compared with the experimental values. Obviously, the predictions from MNDO[23] and HAM/3[24], as well as from the STO-3G[25] method (the geometries have been optimized by using the MM2 force-field program[26]) are in good agreement with the experiment. It is not unusual[27] that MNDO absolute energies are too high by about 1 eV, the STO-3G values too low by 1–2 eV. Yet, orbital sequences and energetic splittings are reproduced in a rather satisfying way.

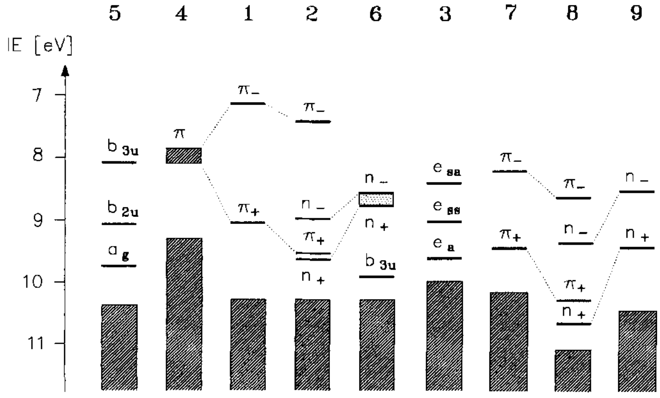


Figure 2. Correlation of PE data of **1**–**9**

Disecododecahedradiene 1, Disecoene 4 and Diene 7

Disecoene **4** gives rise to a well-separated π-ionization band with vibrational fine structure ($\tilde{\nu}$ = 1200 cm^{-1}), the 0,0 and 0,1 transition being of comparable intensity. Taking the 0,1 component of the progression as reference maximum I_1^m the introduction of a second additional π bond (as in **1**) should result in *one* π band at ca. 8.2 eV *if no interaction is possible.* The experimental findings are excitingly different: Compared with the spectrum of monoene **4**, the spectrum of diene **1** exhibits two π-ionization events at 7.12 and 9.03 eV, respectively, i.e. an energetic splitting ΔI_π = 1.91 eV. This is – as will be detailed below – by far the largest π,π splitting measured hitherto in a nonconjugated diene. In view of this record value and of the unique topology of the involved framework, the PE spectrum of **1** will be discussed in some detail.

Table 1. Comparison of experimental ionization energies I_j^m with calculated orbital energies ε_j (all energy values given in eV)

Compound	Ass.	MNDO $-\epsilon_j$	HAM/3 $-\epsilon_j$	STO-3G $-\epsilon_j$	Exp. I_j^m
	π_-	8.92	7.97	5.71	7.12
1	π_+	9.70	9.22	7.62	9.03
	σ	11.46	10.28	9.88	10.38
	π_-	9.17	8.32	6.17	7.48
	n_-	10.37	9.31	8.44	9.05
2	π_+	10.37	9.64	8.74	9.70
	n_+	10.87	9.68	9.22	9.70
	σ	11.65	10.87	10.75	10.43
	e_{sa}	10.20	9.08	7.39	8.40
3	e_{ss}	10.22	9.11	7.98	9.00
	e_a	10.78	9.50	8.54	9.50
	σ	11.09	9.87	9.13	10.00
4	π	9.30	8.66	6.89	7.9-8.3
	σ	11.38	10.21	8.97	9.30
	b_{3u}	10.23	9.56	8.04	8.17
5	b_{2u}	10.88	10.20	9.10	9.05
	a_g	11.20	10.35	9.95	9.76
	σ	11.26	10.70	10.13	10.46
	n_-	10.20	9.11	6.41	8.65-
6	n_+	10.36	9.22	6.58	-8.90
	b_{3u}	10.76	10.06	6.87	10.00
	σ	11.50	10.60	8.15	10.34
	π_-	9.45	8.59	6.94	8.25
7	π_+	10.04	9.19	8.39	9.45
	σ	11.83	11.02	9.35	10.24
	π_-	9.84	8.79	7.26	8.65
	n_-	10.60	9.57	8.58	9.30
8	π_+	10.80	9.68	8.82	10.25
	n_+	11.58	10.24	9.98	10.70
	σ	11.89	11.71	10.15	11.24
	n_-	10.46	9.38	8.06	8.91
9	n_+	10.71	9.53	8.59	9.46
	σ	11.34	10.09	9.30	10.43

Principally, the final energetic splitting ΔI_π between the HOMO (π_-) and the SHOMO (π_+) for **1** may be a result either of OITB or OITS transmission. It has been frequently shown that these two pathways can be distinguished within the frame of chosen suitable models in a procedure proposed by Heilbronner and Schmelzer[28]. In that way, starting from an STO-3G ab initio calculation, first Localized Bond Orbitals (LBOs) are created, according to the localization criterion of Foster and Boys[29]. As shown in Figure 3, the two resulting localized π-orbital combinations are already separated by 1.98 eV, what approximately corresponds to the final, i.e. canonical and experimental result.

The conclusion is justified that it is a *direct* orbital interaction, i.e. through-space homoconjugation, which is responsible for the energetic splitting found in the PE spec-

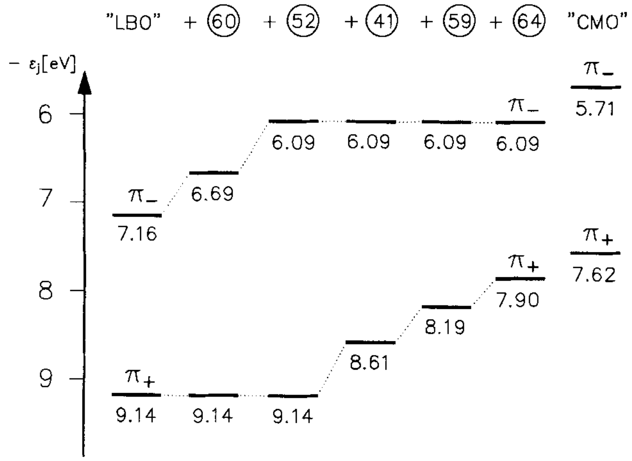
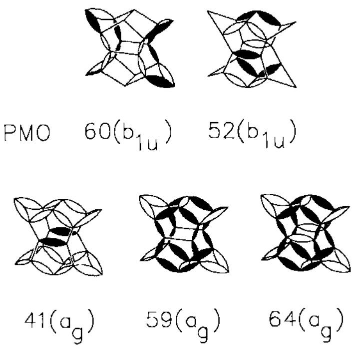


Figure 3. Mixing of PMOs with the π_+ and the π_- combination of **1**

trum of **1**. Indeed, subsequent mixing of the HOMO (π_-, b_{1u}) with the relevant precanonical MOs (PMOs) 60 and 52, both transforming as b_{1u}, and of the SHOMO (π_+, a_g) with PMOs 41, 59, and 64, all transforming as a_g[30], does not change the energetic π,π splitting. Both combinations are destabilized to a similar extent, taking into account the various σ orbitals of corresponding symmetry. The final situation in the canonical MOs (CMOs) excellently reproduces the experimental splitting ΔI_π.

Scheme 5



1,6-Diene **7** represents one "half" of structure **1**; it is not rigid and equilibrates between a closed and an open conformation[20]. Force-field calculations (MM2)[26] and ^{1}H-NMR studies give evidence of the prevalence of the closed conformation with a transannular π,π distance of 310 pm and an interplanary (π,π) angle of 153° (cf. 180° for **1**). In addition, when used as starting geometry for the STO-3G optimization procedure, the results obtained for the closed conformation are in better agreement with the experimental data.

In **7** the HOMO (π_-) and the SHOMO (π_+) are experimentally separated by 1.2 eV, which constitutes an expectedly considerably smaller splitting than in **1**. However, with respect to the interaction pathway, the energetic splitting between the HOMO and the SHOMO is again the outcome of pure OITS.

For the isomeric but rigid 1,6-diene **23** with its closer but not perfectly synperiplanar C=C bonds ($d_{\pi,\pi}$ = 278 pm; ω = 176°) the measured ΔI_π = 1.25 eV has been attributed to 0.9 eV OITS and 0.35 eV OITB[31].

Disecododecahedradienedione 2, Pagodanedione 6 and Diones 8/9

The PE spectrum of the multichromophoric disecodienedione **2** is analyzed by using parent diene **1** and diones **8**/**9** as reference compounds. Interaction of the carbonyl lone pairs in **6** totally occurs through the σ frame, i.e. through bond (OITB). This has been recently demonstrated for the n,n OITB in polycyclic 1,5-diketones[17c], such as the "half" dione **9**. Whereas the PE spectrum of the latter exhibits two distinct signals separated by 0.55 eV, OITB between the lone pairs in pagodanedione **6** results in a broad, hardly resolved band, "hiding" the n_- and the n_+ combination and probably a third band originating from the b_{3u} Walsh orbital of the cyclobutane fragment. According to the calculations an energetic splitting ΔI_n of 0.1−0.2 eV has to be assumed which is to small to be identified. As a consequence, a combination of both effects, OITS of the π MOs and OITB of the n MOs, is expected in the "mixed" dienedione **2**. However, it should be noted that, because of the molecular symmetry (C_{2v}), mixing is only allowed between the π_- and n_+ MO, both transforming as b_2; $\pi_+(a_1)$ and $n_-(a_2)$ have to be assigned to different irreducible representations. The resulting orbital sequence in dienedione **2** is shown in Figure 4, and the n and π orbitals are illustrated schematically as semilocalized symmetry-adapted combinations in Scheme 6.

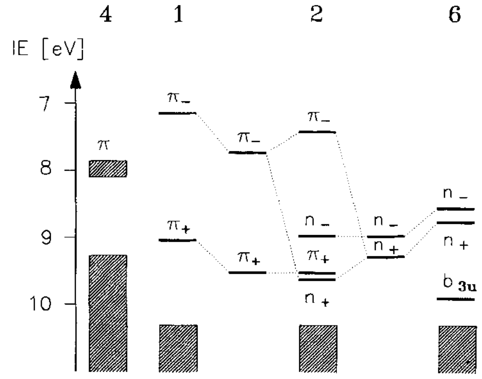
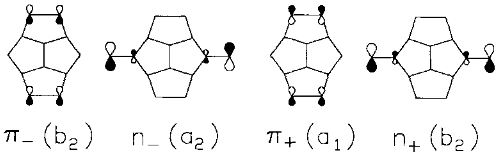


Figure 4. Simplified correlation diagram for **1**, **2**, and **4**−**6**

Scheme 6



Assuming that all four MOs in **2** are inductively stabilized [the inductive stabilization energy can conveniently be derived from the noninteracting orbitals $n_-(a_2)$ and $\pi_+(a_1)$], mixing of $\pi_-(b_2)$ with $n_+(b_2)$ results in a destabilization of the HOMO (π_-), whereas the symmetrical lone-pair combination $n_+(b_2)$ is shifted to higher ionization energies. The π,π splitting ΔI_π is consequently magnified up to a new record of 2.2 eV and the n,n splitting ΔI_n to 0.5 eV. Furthermore, the n_+ and π_+ MOs are now very close or identical in their ionization energies, which explains the missing of a fourth band and the increase in intensity of the third band detected in the PE spectrum of **2** at 9.70 eV. According to this assignment, which has been reproduced best by ab initio STO-3G and HAM/3 calculations, the combined effects of OITS and OITB in the multichromophoric dienedione **2** cause an energetic π,π splitting ΔI_π even larger by some 0.3 eV than in disecodiene **1**.

The interpretation derived for the spectrum of **2** holds also for that of dienedione **8**. In line with the larger transannular π,π distance of 350 pm (MM2) the initial π,π splitting ΔI_π is found to be smaller than in the disecodienedione **2**.

In **8**, as a result of the destabilization of the π_- combination, the π,π splitting ΔI_π of 1.20 eV determined for diene **7** is increased by a similar amount as in **2** (0.4 eV) to 1.60 eV. Stabilization of the n_+ MO leads to a respectable energy difference ΔI_n of 1.40 eV.

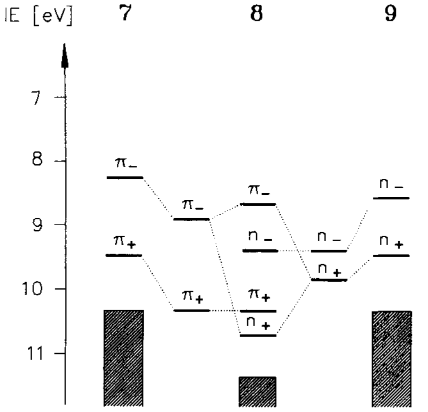


Figure 5. Simplified correlation diagram for **7**–**9**

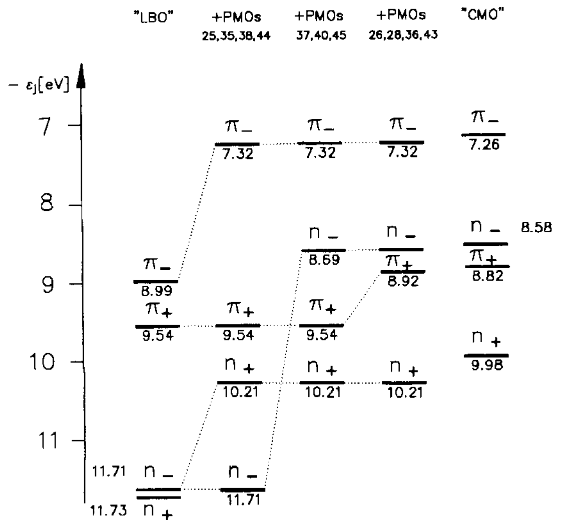
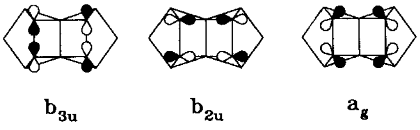


Figure 6. Mixing of PMOs with the π_+/π_- and n_+/n_- combinations of **8**

Pagodane (5)

The low-energy part of the PE spectrum of **5** consists of several well-defined σ-ionization events. According to the calculations and symmetry considerations the two bands at 8.17 and 9.05 eV, respectively, can be assigned to the topmost Walsh orbitals of the cyclobutane fragment. In **5** this cyclobutane ring is forced to be planar. Because of its D_{2h} symmetry, the two formerly degenerate e_u orbitals of planar cyclobutane itself[32] split into a HOMO (b_{3u}) and a SHOMO (b_{2u}) separated by 0.8 eV. The third band, observed at 9.76 eV, then corresponds to the a_g Walsh orbital, and is destabilized by 2.7 eV, when compared to a value of 12.5 eV found in cyclobutane itself[32].

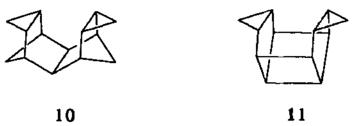
Scheme 7



Dihomodisecododecahedradiene 3

In the PE spectrum of **3**, the dicyclopropanated diene **1**, the first band seems to consist of two ionization events. According to calculations, these can be assigned to the symmetrical and the antisymmetrical combinations of the e_s Walsh orbitals, whereas the corresponding combinations of the e_a Walsh orbitals ionize at higher energies (around 10 eV). Apparently, no further energetic splitting caused by OITS or by OITB between the two subchromophores is observable in the experimental spectrum. At a transannular distance of 317 pm between the inner cyclopropane carbon atoms (X-ray)[14] the extension of the Walsh orbitals is not sufficient to provoke a measurable interaction. In fact, only a small through-bond interaction is indicated by theory.

Scheme 8



10 **11**

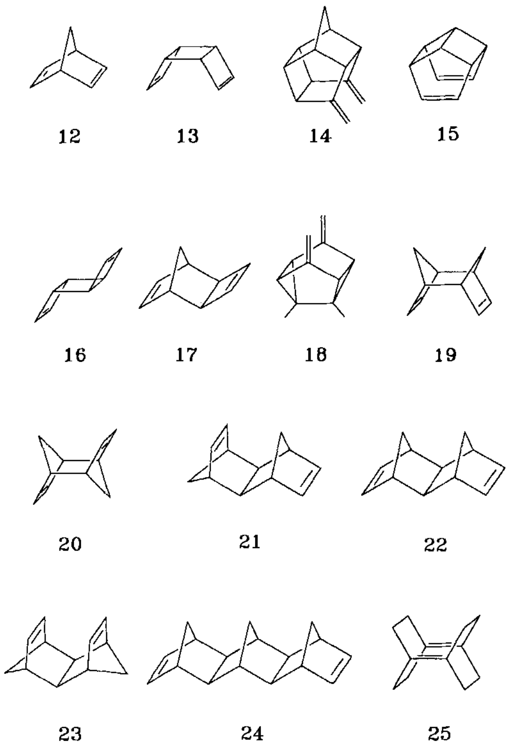
This is not an unexpected finding. He(I_α)-PE spectra of related dicyclopropanated compounds, for instance **10**[12,13] and **11**[33], exhibit a very similar pattern with broad, poorly resolved bands at lower energies. Especially the PE spectrum of **10**, a derivative of **23**, shows three ionization events at lower energies (I_1^m = 8.65 eV, I_2^m = 9.50 eV, I_3^m = 9.90 eV) to which the same orbital sequence (e_{sa}, e_{ss}, e_a) as in **3** could be assigned. The corresponding absolute energies are also in good accordance with the present findings for **3**.

To put the interaction parameters of the 1,6-dienes **1**/**2** and **7**/**8** into a broader context, we present in Table 2 the known values for selected prototypical (1,4-, 1,5-, 1,6-, 1,8)-dienes (c.f. Scheme 9), which feature chains of varying lengths between their *syn*/*anti*-π bonds. The observed splittings ranging from 0.25 eV for **19**[34] to 1.6 eV for **20**[35] are in some cases largely due to through-space, in others largely to through-bond coupling. Clearly, the through-space homoconjugation in **1**/**2** and **7**/**8** is stronger than in **23**, with 1.26 eV for through-space-dominated interaction the long-time record holder.

Table 2. Energetic splittings ΔI_π of known unconjugated dienes (all energy values given in eV)

Compound	ΔI_π [eV]	Ref.	Compound	ΔI_π [eV]	Ref.
12	0.85	*36*	**19**	0.25	*34*
13	0.36	*37*	**20**	1.60	*35*
14	0.48	*38*	**21**	0.44	*31*
15	0.80	*33*	**22**	0.87	*41*
16	0.97	*37*	**23**	1.26	*31*
17	1.15	*39*	**24**	0.32	*42*
18	1.26	*40*	**25**	$\leq$0.2	*43*

Scheme 9



In this context Wiberg's 1,5-diene **25**[43] with its two-carbon bridges between the π bonds is a remarkable case. Like in **1**/**2**, the π bonds are enforced to be perfectly synperiplanar and are, with an experimental π,π distance of 239 pm, even more proximate than in **1**/**2**. Strong pyramidalization (27.3°; 35.6°) and a shoulder at $\lambda = 235$ nm ($\varepsilon \approx 1500$, cyclohexane) are, inter alia, observables of strong π,π interaction (repulsion). Yet, in **25** through-space and through-bond contributions practically compensate each other and thus the π_+ and π_- combinations are accidentally almost degenerate – giving rise to a well-resolved band at 8.6 eV. From calculations it is concluded, c.f. the situation in the series of bicyclo[2.2.*n*]dienes[36], that ε_{π_+} (ε_{π_-}) decreases (increases) as the π distance is decreased, in line with the cross-ring bonding (antibonding) nature of the respective (π_+/π_-) orbitals.

Résumé

In the nonconjugated 1,6-dienes **1**, **2**, **7**, and **8** an unusually strong through-space-dominated π,π interaction is operative. The π,π splitting of 1.9 eV for disecododecahedradiene **1** is even surpassed by the record number of 2.2 eV for the disecodienedione **2**, for which the interplay between $\pi_-(b_2)$ and $n_+(b_2)$ intensifies the orbital splitting. Thus, ΔI_π in **2** almost equals that in 1,3-butadiene (2.46 eV[44]), the prototype for classical π,π conjugation. Obviously, dienes of type **B** with X,Y chains of varying length constitute highly attractive objects for further elaboration of the interplay between the carbon framework and π,π-homoconjugative interaction. Unfortunately, efforts to prepare the [1.1.0.0]-pagodane (**A**, X = CH$_2$, Y = O) or to transform available [2.2.1.1]/[2.2.2.2]pagodanes (**A**, X = CH$_2$, Y = [CH$_2$]$_2$; X = Y = [CH$_2$]$_2$) into the respective [2.2.1.1]/[2.2.2.2]-dienes **B** have not been successful, yet. The isolation of the disecodienetetrone **B** (X = Y = CO), a promising candidate for the next "record", has so far been thwarted by the extreme propensity for hydrate/acetal formation[45]. Our efforts to analyze OITS effects in secodienes **C** and dodecahedradienes **D** do continue.

This work was supported by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *BASF AG*.

CAS Registry Numbers

1: 107798-67-4 / **2**: 107819-45-4 / **3**: 107819-40-9 / **4**: 107798-68-9 / **5**: 89683-62-5 / **6**: 107819-44-3 / **7**: 60606-96-4 / **8**: 98230-16-1 / **9**: 98230-14-9

---

[1] Dedicated to Prof. *Michael Hanack* on the occasion of his 60th birthday. – Part 76: J. Behr, R. Braun, H.-D. Martin, M. B. Rubin, A. Steigel, *Chem. Ber.* **124** (1991) 814.

[2] [2a] S. Winstein, *Spec. Publ. Chem. Soc.* **21** (1967) 5. – [2b] P. M. Warner in *Topics in Nonbenzoid Aromatic Chemistry*, Hirokawa Publishing Co., Tokyo, 1977, vol. 2, p. 283. – [2c] L. A. Paquette, *Angew. Chem.* **90** (1978) 114; *Angew. Chem. Int. Ed. Engl.* **17** (1978) 106. – [2d] R. F. Childs, M. Mahendran, S. D. Zweep, G. S. Shaw, S. K. Chadda, W. A. Burke, B. E. George, R. Faggiani, C. I. L. Loik, *Pure Appl. Chem.* **58** (1986) 111.

[3] [3a] R. Hoffmann, *Acc. Chem. Res.* **4** (1971) 1. – [3b] H. D. Martin, B. Mayer, *Angew. Chem.* **95** (1983) 281; *Angew. Chem. Int. Ed. Engl.* **22** (1983) 283. – [3c] R. Gleiter, *Angew. Chem.* **86** (1974) 770; *Angew. Chem. Int. Ed. Engl.* **13** (1974) 696. – [3d] R. Gleiter, W. Schäfer, *Acc. Chem. Res.* **23** (1990) 369.

[4] [4a] H. Prinzbach, W.-D. Fessner in *Organic Synthesis – Modern Trends* (O. Chizov, Ed.), p. 43, Blackwell Scientific, Oxford, 1987. – [4b] H. Prinzbach, W.-D. Fessner in *Cage Hydrocarbons* (G. A. Olah, Ed.), p. 353, Wiley, New York, 1990.

[5] J.-P. Melder, R. Pinkos, H. Fritz, H. Prinzbach, *Angew. Chem.* **102** (1990) 105; *Angew. Chem. Int. Ed. Engl.* **29** (1990) 95.

[6] R. Pinkos, J.-P. Melder, H. Prinzbach, *Angew. Chem.* **102** (1990) 102; *Angew. Chem. Int. Ed. Engl.* **29** (1990) 92.

[7] P. R. Spurr, Bulusu A. R. C. Murty, W.-D. Fessner, H. Fritz, H. Prinzbach, *Angew. Chem.* **99** (1987) 486; *Angew. Chem. Int. Ed. Engl.* **26** (1987) 455.

[8] H. Irngartinger, U. Reifenstahl, H. Prinzbach, R. Pinkos, K. Weber, *Tetrahedron Lett.* **31** (1990) 5459.

[9] G. K. Surya, Prakash, W.-D. Fessner, G. A. Olah, G. Lutz, H. Prinzbach, *J. Am. Chem. Soc.* **111** (1989) 746.

[10] H. Prinzbach, Bulusu A. R. C. Murty, W.-D. Fessner, J. Mortensen, J. Heinze, G. Gescheidt, F. Gerson, *Angew. Chem.* **99** (1987) 488; *Angew. Chem. Int. Ed. Engl.* **26** (1987) 475.

[11] [11a] G. K. S. Prakash, K. V. Krishnamurthy, R. Herges, R. Bau, H. Yuan, G. A. Olah, W.-D. Fessner, H. Prinzbach, *J. Am. Chem. Soc.* **108** (1986) 836. – [11b] T. Drewello, W.-D. Fessner, A. I. Kos, C. B. Lebrilla, H. Prinzbach, P. v. R. Schleyer, H. Schwarz, *Chem.*

Ber. **121** (1988) 187. — [11c] G. A. Olah in *Cage Hydrocarbons* (G. A. Olah, Ed.), p. 103, Wiley, New York, 1990.

[12] G. Sedelmeier, *Dissertation,* Univ. Freiburg, 1978.

[13] H. Prinzbach, G. Sedelmeier, H.-D. Martin, *Angew. Chem.* **89** (1977) 111; *Angew. Chem. Int. Ed. Engl.* **16** (1977) 103.

[14] G. Lutz, W.-D. Fessner, H. Prinzbach, G. Rihs, manuscript in preparation; G. Lutz, *Dissertation,* Univ. Freiburg, 1990.

[15] σ,σ and π,σ homoconjugation is of long-standing interest to us in connection with its relevance to the corresponding intramolecular $[\pi 2 + \sigma 2]/[\sigma 2 + \sigma 2]$ photocycloaddition reactions[13,16].

[16] [16a] H. Prinzbach, W. Eberbach, G. von Veh, *Angew. Chem.* **77** (1965) 454; *Angew. Chem. Int. Ed. Engl.* **4** (1965) 436. — [16b] H. Prinzbach, W. Eberbach, *Chem. Ber.* **101** (1968) 4083. — [16c] H. Prinzbach, W. Eberbach, G. Philippossian, *Angew. Chem.* **80** (1968) 910; *Angew. Chem. Int. Ed. Engl.* **7** (1968) 887. — [16d] H. Prinzbach, M. Klaus, *Angew. Chem.* **81** (1969) 289; *Angew. Chem. Int. Ed. Engl.* **8** (1969) 276. — [16e] H. Prinzbach, M. Klaus, M. Mayer, *Angew. Chem.* **81** (1969) 902; *Angew. Chem. Int. Ed. Engl.* **8** (1969) 883. — [16f] M. Klaus, H. Prinzbach, *Angew. Chem.* **83** (1971) 292; *Angew. Chem. Int. Ed. Engl.* **10** (1971) 273. — [16g] H. Prinzbach, D. Hunkler, *Chem. Ber.* **106** (1973) 1804. — [16h] G. Sedelmeier, H.-D. Martin, H. Prinzbach, *Chimia* **33** (1979) 329. — [16i] H. Prinzbach, H.-P. Schal, G. Fischer, *Tetrahedron Lett.* **24** (1983) 2147. — [16j] c.f. K. Hassenrück, H.-D. Martin, B. Mayer, T. Urbanek, T. Zirwes, R. Walsh, H.-D. Beckhaus, *Chem. Ber.* **120** (1987) 177.

[17] [17a] H.-D. Martin, B. Albert, H.-J. Schiwek, *Tetrahedron Lett.* **1979**, 2347. — [17b] H. J. Altenbach, D. Constant, H.-D. Martin, B. Mayer, M. Müller, E. Vogel, *Chem. Ber.* **124** (1991) 791. — [17c] B. Albert, D. Elsässer, D. Heckel, S. Kopmeier, H.-D. Martin, B. Mayer, T. J. Chow, T.-K. Wu, S.-K. Yeh, *Chem. Ber,* **124** (1991) 803.

[18] T. Koopmans, *Physica* **1** (1934) 104.

[19] W.-D. Fessner, G. Sedelmeier, P. R. Spurr, G. Rihs, H. Prinzbach, *J. Am. Chem. Soc.* **109** (1987) 4626.

[20] [20a] Bulusu A. R. C. Murty, P. R. Spurr, R. Pinkos, C. Grund, W.-D. Fessner, D. Hunkler, H. Fritz, W. R. Roth, H. Prinzbach, *Chimia* **41** (1987) 32. — [20b] J. P. Melder, F. Wahl, H. Fritz, H. Prinzbach, *Chimia* **41** (1987) 426.

[21] G. Sedelmeier, W.-D. Fessner, R. Pinkos, C. Grund, Bulusu A. R. C. Murty, D. Hunkler, G. Rihs, H. Fritz, C. Krüger, H. Prinzbach, *Chem. Ber.* **119** (1986) 3442.

[22] All PE spectra were recorded with a UPG-200 (Leybold-Heraeus) spectrometer.

[23] M. S. J. Dewar, W. Thiel, *J. Am. Chem. Soc.* **99** (1975) 4899.

[24] L. A. Asbrink, C. Fridh, E. Lindholm, *Chem. Phys. Lett.* **52** (1977) 61.

[25] W. J. Hehre, R. F. Stewart, J. A. Pople, *J. Chem. Phys.* **51** (1969) 2657.

[26] [26a] N. L. Allinger, *J. Am. Chem. Soc.* **99** (1975) 8127. — [26b] N. L. Allinger, Y. Yuh, *QCPE* **13** (1987) 395. — [26c] J. T. Sprague, J. C. Tai, Y. Yuh, N. L. Allinger, *J. Comput. Chem.* **8** (1987) 581.

[27] H.-D. Martin, B. Mayer, R. W. Hoffmann, A. Riemann, P. Rademacher, *Chem. Ber.* **118** (1985) 2514.

[28] [28a] E. Heilbronner, A. Schmelzer, *Helv. Chim. Acta* **58** (1975) 936. — [28b] G. Bieri, E. Heilbronner, A. Schmelzer, *Helv. Chim. Acta* **60** (1977) 2234.

[29] [29a] J. M. Foster, S. F. Boys, *Rev. Mod. Phys.* **32** (1969) 300. — [29b] M. Scholz, H. J. Köhler, *Quantenchemie,* vol. 3, p. 384, Dr. Alfred Hüthig Verlag, Heidelberg, 1981. — [29c] D. Peeters, QCPE Nr. 330, *QCPE Newsletters* **57** (1977) 19.

[30] Contribution of the individual PMOs in **1**: π_-: PMO 60 (53%), PMO 52 (47%); π_+: PMO 41 (43%), PMO 59 (33%), PMO 64 (24%).

[31] H.-D. Martin, R. Schwesinger, *Chem. Ber.* **107** (1974) 7599.

[32] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata, *Handbook of He(I) Photoelectron Spectra of Fundamental Organic Molecules,* p. 62, Halsted Press, New York, 1981.

[33] J. Spanget-Larsen, R. Gleiter, G. Klein, C. W. Doecke, L. A. Paquette, *Chem. Ber.* **113** (1980) 2120.

[34] L. A. Paquette, C. W. Doecke, G. Klein, *J. Am. Chem. Soc.* **101** (1971) 7599.

[35] W. Grimme, L. Schumachers, R. Gleiter, K. Gubernator, *Angew. Chem.* **93** (1981) 98; *Angew. Chem. Int. Ed. Engl.* **20** (1981) 113.

[36] [36a] P. Bischof, J. Hashmall, E. Heilbronner, V. Hornung, *Helv. Chim. Acta* **52** (1969) 1745. — [36b] E. Heilbronner, H.-D. Martin, *Helv. Chim. Acta* **55** (1972) 1490.

[37] R. Gleiter, E. Heilbronner, M. Hekmann, H.-D. Martin, *Chem. Ber.* **106** (1973) 28.

[38] A. P. Marchand, C. Huang, R. Kaya, A. D. Baker, E. D. Jammis, D. A. Dixon, *J. Am. Chem. Soc.* **109** (1987) 7095.

[39] F. Broglie, W. Eberbach, E. Haselbach, E. Heilbronner, V. Hornung, D. M. Lemal, *Helv. Chim. Acta* **56** (1973) 1933.

[40] R. Gleiter, G. Jähne, *Tetrahedron Lett.* **24** (1983) 5063.

[41] M. N. Paddon-Row, H. K. Patney, R. S. Brown, K. N. Houk, *J. Am. Chem. Soc.* **103** (1981) 5575.

[42] [42a] P. E. Schipper, M. N. Paddon-Row, *Aust. J. Chem.* **35** (1982) 1755. — [42b] M. N. Paddon-Row, *Acc. Chem. Res.* **15** (1982) 245.

[43] E. Honegger, E. Heilbronner, K. Wiberg, *J. Electron Spectrosc. Rel. Phenom.* **31** (1983) 369.

[44] [44a] P. Bischof, E. Haselbach, E. Heilbronner, *Angew. Chem.* **82** (1970) 952; *Angew. Chem. Int. Ed. Engl.* **9** (1970) 953. — [44b] R. Gleiter, *Top. Curr. Chem.* **86** (1979) 222.

[45] H.-P. Melder, H. Prinzbach, *Chem. Ber.* **124** (1991) 1271.

[264/91]