Small and Medium Rings, 78[1)]

Cage Dimers of Norbornadiene with Perpendicular Arrangement of Subchromophores: Orbital Interaction in the Heptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]tetradecane System

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Received July 3, 1991

Key Words: Polyquinanes / Norbornadiene dimers / Orbital interaction, through-bond / PE spectroscopy / Orbitals, precanonical / Switches, molecular

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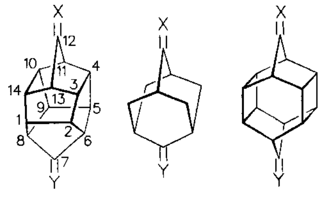
The syntheses of functionalized norbornadiene dimers **1** are described. These cage compounds feature remarkably high D_{2d} symmetry as regards the dimethylene and dioxo derivatives **1d** and **1e**. On the other hand, the mixed enone compound **1f** behaves differently: π_{CC} and lone-pair n_{CO} orbitals mix strongly with each other, albeit only by means of the intervening five-bond σ system. All theoretical conclusions have been verified by using PE spectroscopy. A comparison is made between systems **1** and the geometrically similar adamantanes **2**, on the one hand, and the attractive but still unknown derivatives of garudane **3** on the other hand. The latter exhibit the interesting parallel topology of suitable chromophores, thus making these polycycles **3** desirable candidates for transmission studies.

The chemistry of cage-shaped hydrocarbons (polyhedranes, prismanes, polyquinanes, adamantanes) and their derivatives has attracted wide interest among both, theoretical and synthetic chemists[2)]. These aesthetically fascinating compounds continue to represent a synthetic challenge because of their increasing practical importance. For instance, their application as energy materials[3)] and as medicinal substances[4)], e.g. antiviral agents[5)], has been recently discussed. Besides these practical purposes cage-shaped hydrocarbons often provide conformationally fixed carbocyclic skeletons with a defined inherent symmetry. In this regard they become particularly interesting objects of spectroscopical and theoretical studies.

Scheme 1



1 2 3

a: X = Y = H_2; **b**: X = O, Y = H_2; **c**: X = CH_2, Y = H_2; **d**: X = Y = O; **e**: X = Y = CH_2; **f**: X = CH_2; Y = O; **g**: X = OCH_2CH_2O, Y = O; **h**: X = OCH_2CH_2O, Y = H_2

However, syntheses of such cage compounds are sometimes tedious since assembling a highly compact structure is an entropy-disfavored process. One example how to overcome this difficulty by organometallic means is the efficient formation of the eight-membered polyquinane **1a** (heptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]-tetradecane[6)]) which is commonly referred to as HCTD. The octaquinane **1a** is formed in one step by metal-assisted dimerization of norbornadiene (NBD). This was first observed in 1961[7)] and since then has been studied extensively[8)]. An ordinary dimerization of NBD generally produces several isomers simultaneously[9)]. Only a few stereospecific reactions have been known[10)]. Recently, one of us reported a stereospecific *endo-cis-endo* coupling of NBD in the presence of hexacarbonylmolybdenum[11)]. The resulting cage dimer **1a** is formed exclusively in a yield of 26%. Dimerization of 7-*tert*-butoxynorbornadiene[12)] and related NBD derivatives[13)] gave access to HCTD derivatives oxygenated in the 7,12-position[14)]. In the presence of hexacarbonylmolybdenum the dimer of *tert*-butoxynorbornadiene was also formed in a stereospecific reaction[15)], thus facilitating the syntheses of monoketone **1b** and diketone **1d**[16)].

In the present communication we will report on the preparation of the corresponding olefines **1c** and **1e**, respectively, as well as of the "mixed" enone **1f**, in order to provide a series of HCDT derivatives with a common structural feature: Due to the stereospecific cross dimerization of NBD the carbocyclic skeletons of **1a**–**1f** show the remarkable D_{2d} symmetry. As a consequence, the two double bonds in

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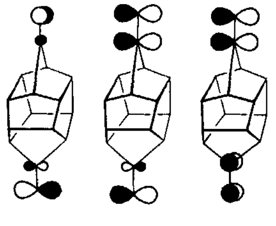
the bifunctionalized compounds **1d** and **1e** are chemically equivalent, the π orbitals, however, are orientated perpendicular to each other. This contrasts with the mutual alignment of π and n orbitals in **1f** which is a parallel one.

Scheme 2



1d (D_{2d}) 1f (C_{2v}) 1e (D_{2d})

This particularity should have considerable influence on any possible (orbital) interaction between the two subchromophores, especially on that transmitted through the HCTD σ skeleton, i.e. Orbital Interaction through Bond (OITB)[17].

Generally interested in transannular (orbital) interaction in multichromophoric systems[18], we therefore decided to study compounds **1a**–**1f** by He(I_α)-PE spectroscopy. A convenient measure for such interactions is the energetic difference between the formerly degenerate MOs. If the validity of Koopmans' approximation is assumed[19], the effect can be directly observed in the PE spectra as a measurable energetic splitting.

Polycyclic organic molecules having D_{2d} symmetry are comparatively rare. Yet, another series of compounds which also provides a molecular framework of D_{2d} symmetry is that of adamantanes **2a**–**2f**. These promise to be excellently suited as reference compounds and, with the exception of **2e** and **2f**, have been extensively studied before[20]. In the present study the missing PE data of diene **2e** have been recorded, unfortunately, those of enone **2f** are still not available. The PE spectra of **2a**–**2e** will help to discuss and interpret our experimental findings for the HCTD system.

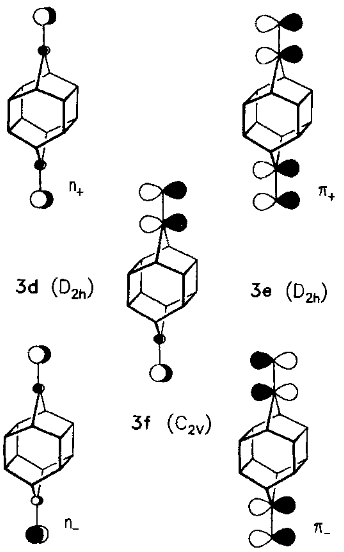
Whilst HCTD (**1a**) represents the D_{2d} dimer of norbornadiene, its D_{2h} dimer is realized in the fascinating cage compound **3a**. Although this hydrocarbon **3a**, commonly referred to as "garudane"[21], has been recently prepared[22], syntheses of the required derivatives (**3b**–**3f**) are still unknown. In contrast to **1**, the arrangement of the subchromophores in the garudane system **3** is a parallel one.

Orbital interaction in **3d** and **3e** is expected to be much more pronounced. Although it can at the moment only be predicted by computational methods, its discussion appears to be worthwhile. In the present report this will be accomplished by using force-field, semiempirical and ab initio methods.

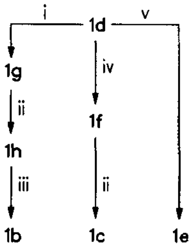
Syntheses

The cage-shaped hydrocarbon **1a** has been prepared by $Mo(CO)_6$-catalyzed stereospecific dimerization of norbornadiene as previously described[11]. The synthesis of diketone **1d** using *tert*-butoxynorbornadiene as starting compound has also been reported earlier[14,16]. The corresponding monoketone **1b**, monoene **1c**, diene **1e**, and the mixed enone **1f** have been synthesized as outlined in Scheme 4.

Scheme 3



Scheme 4



i) $HOCH_2CH_2OH$; *p*TSA; C_6H_6. – ii) $(HOCH_2CH_2)_2O$; KOH; N_2H_2. – iii) H_2SO_4; CH_2Cl_2. – iv) $(Ph_3PCH_3)^+Br^-$ (1 equiv.); *n*BuLi; THF; −70°C. – v) $(Ph_3PCH_3)^+Br^-$ (2 equiv.); *n*BuLi; THF; 0°C.

The reaction of a benzene solution of **1d** with ethylene glycol (1 equivalent) in the presence of catalytic amounts of *p*-toluenesulfonic acid in a Dean-Stark apparatus afforded the corresponding mono(ethylene acetal) **1g**. Wolff-Kishner reduction of the ketone carbonyl group in **1g** followed by acid hydrolysis of the intermediate **1h** afforded monoketone **1b**. Wittig reaction of **1d** with one equivalent of methylenetriphenylphosphorane yielded the mixed enone **1f**, which was converted into monoene **1c** by Wolff-Kishner reduction. The reaction of two equivalents of the ylide with dione **1d** resulted in the formation of diene **1e**[23,24]. The synthesis of diene **2e** was effected according to the known procedure[25].

PE Spectroscopy

The He(I_α)-PE spectra of **1a**–**1f** are illustrated in Figure 1, and the relevant band energies of all six compounds are graphically correlated in Figure 2. In Table 1 the corresponding experimental ionization energies I_j^m are compared with the theoretical orbital energies ε_j resulting from semiempirical and ab initio calculations.

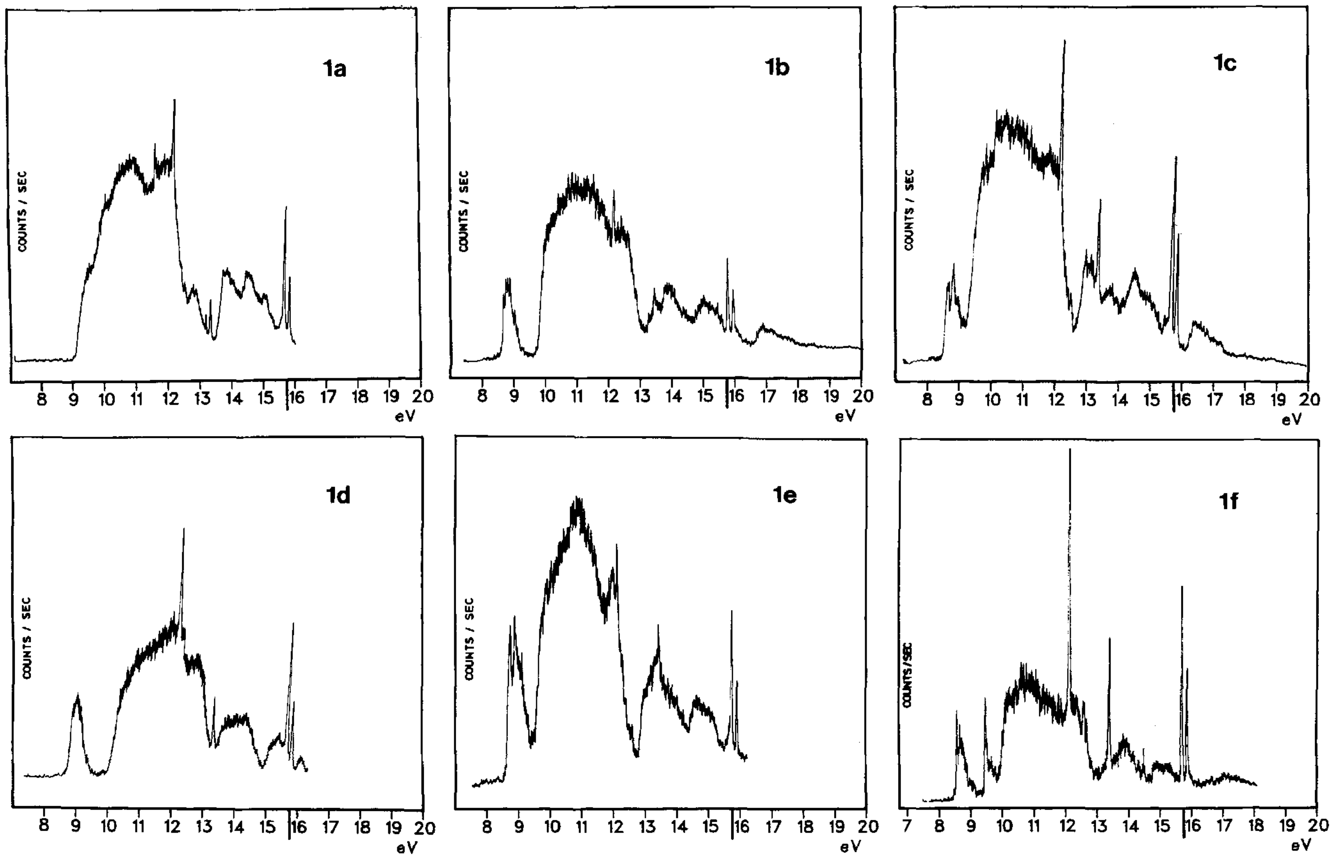


Figure 1. He(I_α)-PE spectra of **1a**–**1f** (calibration gases: Ar: 15.76, 15.94 eV; Xe: 12.13, 13.45 eV)

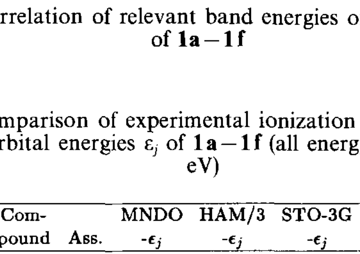


Figure 2. Correlation of relevant band energies of the PE spectra of **1a**–**1f**

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

Compound	Ass.	MNDO $-\epsilon_j$	HAM/3 $-\epsilon_j$	STO-3G $-\epsilon_j$	Exp. I_j^m
1a	σ	11.34	10.41	9.10	9.63
1b	n	10.34	9.05	8.06	8.77
	σ	11.76	10.72	10.12	10.21
1c	π	9.79	9.07	7.76	9.00
	σ	11.40	10.43	9.84	9.86
1d	n_+	10.54	9.22	8.22	–
	n_-	10.54	9.22	8.22	9.10
	σ	12.15	11.07	10.55	10.67
1e	π_-	9.80	9.03	7.80	–
	π_+	9.80	9.03	7.80	8.90
	σ	11.42	10.43	9.94	10.00
1f	$n+\pi$	9.95	8.96	7.72	8.65
	$n-\pi$	10.43	9.28	8.50	9.55
	σ	11.76	10.64	10.04	10.40

The lower energetic part of the PE spectrum of **1a** only exhibits a broad band of unresolved σ-ionization events of the hydrocarbon with a measurable "σ onset" of $I^m \approx 9.63$ eV, whereas the spectra of **1b**–**1e** each show one first band which is clearly separated from the σ ionizations. Assuming the validity of Koopmans' approximation[19], we can assign these ionization energies I_j^m to the orbital energies ε_j of the corresponding HOMOs, which are represented either by lone-pair (n) (in ketones **1b** and **1d**) or by π orbitals (in olefines **1c** and **1e**). It has to be noted that the HOMO of diketone **1d** is stabilized by 0.33 eV compared to monoketone **1b**. In contrast, the first ionization energies of the two olefines **1c** and **1e** only differ by 0.1 eV, and, moreover, both bands exhibit the same vibrational fine structure ($\tilde{\nu} = 1200$ cm^{-1}).

Finally, the PE spectrum of the mixed enone **1f** shows two distinct bands separated by 0.90 eV. But orbital assignment of these two ionization events is not unambiguous. It will therefore be discussed in more detail by means of computational methods.

Discussion

Inspection of Table 1 shows that predictions on the basis of MNDO[26] and HAM/3[27], as well as of the STO-3G method[28] are in good agreement with the experiment. It is not unusual[29] that MNDO overestimates the absolute energies by about 1 eV, whereas STO-3G lowers them by 1–2 eV. But energetic differences and the orbital assignment are reproduced in a rather satisfying way. For all compounds calculations were based on starting geometries which have been optimized by using the MM2 force-field program[30]. For **1a**, **1b**, and **1f** these results did not differ significantly when the corresponding X-ray crystallographic structures[15a,24] were used.

As shown in Table 2 the measured "σ onset" of HCTD (**1a**) corresponds well with that found in adamantane (**2a**), and, owing to their molecular size, both compounds ionize at low energies.

Table 2. Comparison between experimental ionization energies I_j^m of **1a** – **1f** and their analogs **2a** – **2f** (all energy values given in eV)

	1	2	Ass.
a	9.63	9.44	σ
b	8.77	8.88	n
	10.21	10.00	σ
c	9.00	8.89	π
	9.86	–	σ
d	9.10	9.25	n,n
	10.67	–	σ
e	8.92	8.72	π,π
	10.00	10.05	σ
f	8.70	–	$n+\pi$
	9.55	–	$n-\pi$
	10.40	–	σ

Ketones 1b and 1d

As mentioned above, the PE spectrum of monoketone **1b** exhibits a single band clearly separated from the signals resulting from the σ-ionization events. Its ionization energy I_1^m = 8.77 eV is slightly decreased compared to that of the corresponding adamantanone **2b** (I_1^m = 8.88 eV) and has to be assigned to the lone-pair HOMO. Its relative low energy may be explained by a strong inductive and hyperconjugative participation of adjacent σ bonds which is also experimentally indicated by the broadened band shape in the PE spectrum of **1b**. In addition, it has been previously shown[31] that the nonbonding ionization energy of alicyclic ketones decreases as the size of the molecular skeleton increases.

Introduction of a second carbonyl group in **1d** does not lead to a second, additional ionization band. Apparently, the HOMO and SHOMO n MOs must be degenerate ($I_1^m = I_2^m$ = 9.10 eV). In view of the perpendicular arrangement of the two n orbitals in **1d** this degeneracy is not at all accidental and has been confirmed best by our calculations. Yet, introduction of the second carbonyl group causes the ionization band to be shifted to higher energies by 0.3 – 0.4 eV. This finding may be explained by a less significant destabilization of the degenerate lone-pair combinations due to both the reduced number of appropiate symmetry-adapted σ orbitals and the lower energy of them, i.e. these stabilized σ orbitals are not as conducive to inductive participation as the original ones in ketone **1b**. The same inductive stabilization as well as degeneracy is also found in adamantandione **2d** ($I_1^m = I_2^m$ = 9.25 eV). Any n,n orbital interaction is strictly inhibited by D_{2d} symmetry.

In contrast to diketone **1d** our preliminary calculations predict a considerable energetic splitting $\Delta I_{n,n}$ of 0.8 eV between a HOMO (n_+) and a SHOMO (n_-) combination in garudandione **3d** (cf. Table 3), thus indicating that OITB is playing an important role in the D_{2h}-symmetrical carbocyclic skeleton of the garudane system **3**.

Table 3. Calculated orbital energies ε_j of **3a** – **3f** (all energy values given in eV)

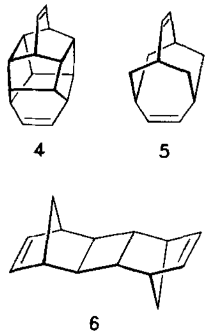
Compound	Ass.	MNDO $-\epsilon_j$	HAM/3 $-\epsilon_j$	STO-3G $-\epsilon_j$
3a	σ	10.72	9.51	8.64
3b	n	10.18	8.96	7.79
	σ	11.04	9.74	8.95
3c	π	9.83	9.23	7.88
	σ	10.73	9.47	8.74
3d	n_+	10.26	9.00	7.70
	n_-	10.67	9.33	8.51
	σ	11.36	10.00	9.34
3e	π_-	9.78	9.11	8.14
	π_+	9.83	9.20	8.25
	σ	10.63	9.32	8.91
3f	n	10.00	8.93	7.88
	π	10.21	9.36	8.02
	σ	11.01	9.70	9.00

Olefins 1c and 1e

A π-ionization band with a characteristic vibrational fine structure ($\tilde{\nu}$ = 1200 cm^{-1}) is measured in the PE spectrum of monoene **1c**. This vibrational frequency can be assigned readily to the C=C stretching mode for the ionic state. It has been shown previously[32] that 1,1-dimethyl substitution on ethylene causes a decrease in I_1^m from 10.56 to 9.21 eV. The HCTD (**1**) moiety would be expected to cause an even larger decrease in the π-ionization potential of ethylene because of the size of **1** and because of the added strain which would be introduced at the sp^2 carbon atom of the double bond. This is corroborated for the π-ionization energy I_1^m = 9.0 eV in methylene-HCTD **1c**. The PE spectrum of diene **1e**, again, only exhibits one ionization band for the two degenerate π MOs, and its vibrational fine structure is exactly the same as in monoene **1c**. Introduction of the second methylene group has virtually no influence on the π-ionization energy. In best accordance with the findings for dimethyleneadamantane **2e** only an insignificant destabilization of 0.1 – 0.2 eV is observed. This suggests that the π MOs participate less in interactions with appropiate σ orbitals than do the lone-pair MOs in diketones **1d** and **2d**. In addition, although it may be considered as a "stretched allene" no Jahn-Teller splitting is measured in the PE spectrum of **1e**. Symmetrical molecules like methane (T_d) or allene (D_{2d})[33] exhibit such vibronic splitting. Yet, the Jahn-Teller effect has already been negated for adamantane (**2a**) and a variety of its derivatives with respect to their molecular rigidity[20]. Orbital interactions in compounds containing perpendicularly arranged π systems have also been discussed by Bischof and Gleiter[34].

Recently, we have reported the synthesis of diene **4** which represents the D_{2d} dimer of barrelene[35]. In this heptacyclodecane derivative the two endocyclic double bonds, again, have a perpendicular arrangement. Therefore, degeneracy of the π MOs is expected. Inspection of the PE spectrum of its adamantane analog **5**[36] confirms this assumption best, for we could only find one broad π-ionization band at I_1^m = 8.90 eV. Because of the perfect accordance between the adamantane (**2**) and the HCTD (**1**) system, as shown above in Table 2, no spectacular findings should therefore be expected for the PE data of the barrelene dimer **4**.

Scheme 5



4 **5**

6

In dimethylenegarudane **3e**, the D_{2h}-symmetrical analog of **1e**, π,π-orbital interaction should not be forbidden. Indeed, $\Delta I_{\pi,\pi}$ is calculated to be ca. 0.12 eV, separating the HOMO (π_-) and the SHOMO (π_+). This π,π through-bond coupling is a reasonable value for a topology with five intervening bonds, but it is much weaker than the calculated value of 0.41 eV for the stretched NBD dimer **6**, which probably is due to the ideal zigzag topology of its σ framework.

A comparison of calculated n,n and π,π through-bond coupling in **3d** and **3e**, respectively, once again reveals that the lone-pair n orbitals are much more conducive to mixing with appropriate σ MOs than the π orbitals. This interpretation is also confirmed by the detailed computational analysis of enone **1f**, as discussed below.

Enone 1f

A most interesting situation is realized in the mixed enone **1f**. Here, the axes of n and π MOs in the two subchromophores are arranged parallel to each other both transforming as b_1 in the C_{2v} point group. As a consequence, through-bond coupling in **1f** should become probable or, at least, allowed. At first view, it is not quite clear how to assign the first two bands (I_1^m = 8.70; I_2^m = 9.55 eV) which are clearly separated by 0.85 eV. In the absence of an unambiguous empirical interpretation this experimental finding has to be discussed in some detail by using computational methods.

It has frequently been demonstrated that individual pathways of orbital interaction can be successfully distinguished in a procedure proposed by Heilbronner and Schmelzer[37]. 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[38]. The Hartree-Fock matrix in the basis of LBOs is a non diagonal one; the diagonal elements providing the basis energy of the LBOs. The off-diagonal matrix elements indicate the direct interaction parameters between the corresponding LBOs and thus give evidence about any through-space interaction (OITS). As expected, in **1f** no direct through-space interaction is detected between the lone-pair and the π MO. The LBO basis energy of the n orbital (−11.56 eV) and that of the π MO (−8.73 eV) are largely separated by 2.83 eV, the lone-pair energy being much closer to the σ LBO basis energies. In order to explain through-bond interaction (OITB) mixing of the localized subchromophores with relevant σ orbitals is necessary. To detect such relevant σ MOs the LBOs are transformed into new symmetry-adapted, semilocalized MOs. With these as a new basis in the HF matrix all non-diagonal elements in the rows and columns of the n and π orbitals are set to zero. Subsequent diagonalization and transformation provide the so-called Precanonical MOs (PMOs) and, in addition, the corresponding HF matrix relating PMOs to the n and π MO, respectively. In this new matrix all significant non-diagonal elements of the n and π orbitals indicate relevant σ PMOs. These can now be subsequently mixed with the two subchromophores until the final, i.e. canonical energetic situation is reproduced.

As shown in Figure 3 this has been accomplished for enone **1f**. From Table 4 it is evident that it is the localized lone-pair MO that strongly mixes with a few σ PMOs. As a matter of fact only 4 PMOs ($\psi_1 - \psi_4$, cf. Scheme 6) are necessary to reproduce the canonical situation in a satisfying way. It should be noted that all 4 PMOs are transforming as b_1, and, as a consequence, that they can all interact with both the n and the π MO. However, matrix elements are much more important for the lone pair, the self-energy of the latter being much closer to the PMO energy than that of the π MO. Thus, by mixing with $\psi_1 - \psi_4$ the localized n

Table 4. HF matrix elements of relevant PMOs ψ_j of **1f**

	ψ_1	ψ_2	n	ψ_3	ψ_4	π
ψ_1	-13.35	0	0.55	0	0	-1.38
ψ_2	0	-12.39	1.25	0	0	-0.27
n	0.55	1.25	-11.56	-1.71	-2.06	0.03
ψ_3	0	0	-1.71	-11.02	0	-0.81
ψ_4	0	0	-2.06	0	-10.80	0.51
π	-1.38	-0.27	0.03	-0.81	0.51	-8.73

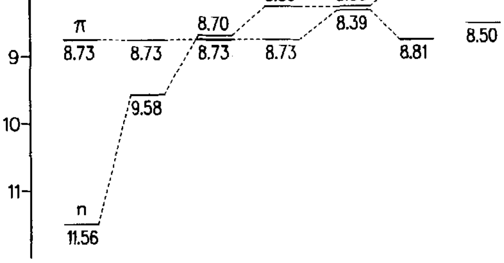
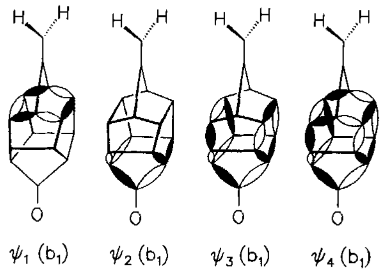


Figure 3. Mixing of relevant PMOs ψ_j with the localized π and n MOs in **1f** (all energy values given in eV)

orbital is destabilized by 3.0 eV and changed into a delocalized n(σ) orbital, whereas the π MO is only raised by 0.34 eV. As shown in Figure 3 (column 5), both are now almost equal in their orbital energies [$\varepsilon_{n(\sigma)} = -8.36$ eV; $\varepsilon_{\pi} = -8.39$ eV] and by subsequently mixing, split into a symmetrical [n(σ) + π] and an unsymmetrical [n(σ) − π] combination at $\varepsilon_1 = -7.89$ and $\varepsilon_2 = -8.81$ eV, respectively. This result reproduces the canonical situation in a satisfying way.

Scheme 6



Conclusion

Previously, we have shown that the recently observed very rapid rates of long-range intramolecular electron-transfer processes in rigid norbornylogous systems are the result of mediating through-bond interactions[39]. Taking into account the results of the present study, the two cage dimers of NBD (**1** and **3**) clearly offer the exciting prospect of investigating two new σ skeletons which could behave like a classical switch, switching orbital interaction either on (**3**) or off (**1**).

This work was supported by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *BASF AG*. A.P.M. thanks the *Air Force Office of Scientific Research* (Grant AFOSR-88-0132) and the *Robert Welch Foundation* (Grant B-963) for financial support of this study. T.J.C. thanks the *Alexander von Humboldt Foundation* for a fellowship during the time of this work.

Experimental

IR: Perkin-Elmer 1330. – ^{1}H and ^{13}C NMR: Jeol FX-900 and Varian VXR-300; chemical shifts (δ values) of ^{1}H were measured downfield from TMS, while those of ^{13}C were obtained by using the central peak of $CDCl_3$ as an internal reference. – MS: Hewlett-Packard 5970 A. – He(I_α) PE: Leybold-Heraeus UPG 200.

7,12-Dimethyleneheptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]*tetradecane* (**1e**): A solution of methyltriphenylphosphonium bromide (800 mg, 2.2 mmol) in dry THF (50 ml) was cooled externally to 0 °C. To this cooled solution under nitrogen was added with stirring a solution of *n*-butyllithium in hexane (2.5 M, 1.0 ml, 2.5 mmol). The resulting red solution was stirred at 0 °C for 0.5 h. A solution of **1d** (212 mg, 1.0 mmol) in dry THF (20 ml) was added to the reaction mixture, and the resulting mixture was stirred at 0 °C for 0.5 h. The cold bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature. The reaction mixture then was poured into hexane (100 ml) and washed with water (3 × 20 ml). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting with hexane. Pure **1e** (140 mg, 67%) was thereby obtained as a colorless microcrystalline solid, m.p. 107–108 °C. – IR (KBr): = 2960 cm^{-1}, 1660. – ^{1}H NMR ($CDCl_3$): δ = 2.55 (m, 8H), 2.62 (m, 4H), 4.45 (m, 4H). – ^{13}C-NMR ($CDCl_3$): δ = 52.85 (d), 52.99 (d), 96.51 (t), 165.08 (s). – MS (70 eV): *m/z* (%) = 209 (16), 208 (91) [M^+], 193 (22), 165 (25), 129 (70), 115 (100).

$C_{16}H_{16}$ (208.3) Calcd. C 92.26 H 7.74
Found C 92.44 H 7.77

12-Methyleneheptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]*tetradecane-7-one* (**1f**): A stirred suspension of methyltriphenylphosphonium bromide (400 mg, 1.1 mmol) in dry THF (50 ml) under nitrogen was cooled to −70 °C by application of an external dry ice/acetone bath. To this cooled solution under nitrogen was added with stirring a solution of *n*-butyllithium in hexane (2.5 M, 0.50 ml, 1.2 mmol). The resulting solution was stirred at −70 °C for 1 h. A solution of **1d** (212 mg, 1.0 mmol) in dry THF (20 ml) was added rapidly. The cold bath was removed, and the stirred reaction mixture was allowed to warm gradually to room temperature during 2 h. Hexane (50 ml) was then added, and the resulting mixture was washed with water (3 × 20 ml). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel by using a hexane → 10% EtOAc/hexane gradient elution scheme. Pure **1f** (140 mg, 67%) was thereby obtained as a colorless microcrystalline solid, m.p. 178–179 °C. – IR (KBr): ṽ = 2990 cm^{-1}, 1745, 1660. – ^{1}H-NMR ($CDCl_3$): δ = 2.34–2.40 (br. s, 2H), 2.56–2.65 (br. s, 2H), 2.72–2.80 (br. s, 4H), 4.53 (m, 2H). – ^{13}C NMR ($CDCl_3$): δ = 47.12 (d), 49.63 (d), 52.26 (d), 54.86 (d), 97.80 (t), 165.41 (s), 216.90 (s). – MS (70 eV): *m/z* (%) = 211 (17), 210 (100) [M^+], 182 (38), 167 (69), 128 (43), 115 (68).

$C_{15}H_{14}O$ (210.3) Calcd. C 85.68 H 6.71
Found C 85.44 H 6.96

7-Methyleneheptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]*tetradecane* (**1c**): A mixture of diethylene glycol (25 ml) and KOH (840 mg, 15.0 mmol) in a round-bottom flask (50 ml) was heated until all of the solid KOH had dissolved. The temperature of the reaction flask was then adjusted to 80 °C, and **1f** (260 mg, 1.24 mmol) was added. To the resulting mixture was added with stirring anhydrous hydrazine (500 mg, 15.0 mmol), and then the temperature of the reaction mixture was increased to 150 °C, and stirring was continued for 4 h. The reaction flask was fitted with a Dean-Stark apparatus, and the reaction temperature was increased to 200–210 °C and was maintained at that temperature for ca. 12 h. The reaction was then allowed to cool gradually to room temperature. Water (25 ml) was added, and the resulting mixture was extracted with hexane (4 × 30 ml). The combined extracts were washed with water (3 × 20 ml). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. Recrystallization of the residue thereby obtained from hexane afforded pure **1c** (202 mg, 83%) as a colorless microcrystalline solid, m.p. 78–79 °C. – IR (KBr): ṽ = 2970 cm^{-1}, 1670, 1300. – ^{1}H-NMR ($CDCl_3$): δ = 1.90 (m, 2H), 2.39–2.68 (m, 12H), 4.45 (m, 2H). – ^{13}C-NMR ($CDCl_3$): δ = 44.32 (t), 49.55 (d), 52.19 (d), 54.07 (d), 54.26 (d), 95.98 (t), 164.67 (s). – MS (70 eV): *m/z* (%) = 197 (13), 196 (77) [M^+], 130 (100).

$C_{15}H_{16}$ (196.3) Calcd. C 91.78 H 8.22
Found C 91.95 H 8.26

Heptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]*tetradecane-7,12-dione Monoethylene Acetal* (**1g**): A mixture of **1d** (1.0 g, 4.7 mmol), ethylene glycol (290 mg, 4.7 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH, catalytic amount) in dry benzene (100 ml) was placed in a round-bottom flask (250 ml) that had been fitted with a condenser and a Dean-Stark apparatus. The reaction mixture was heated to reflux for ca. 12 h, during which time water was removed periodically from the Dean-Stark apparatus. The reaction mixture then was allowed to cool to ambient temperature. The cooled reaction mixture was washed sequentially with 5% aqueous $NaHCO_3$ solution (2 × 10 ml) and water (3 × 20 ml). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel by using a 10→20% EtOAc/hexane gradient elution scheme. Pure **1g** (700 mg, 58%) was thereby obtained as a colorless microcrystalline solid, m. p. 159 – 160°C. – IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1}, 2910, 1740, 1330, 1290, 1215, 1140. – ^{1}H-NMR ($CDCl_3$): δ = 2.15 (m, 2H), 2.32 (m, 2H), 2.62 (m, 4H), 2.83 (m, 4H), 3.94 (m, 4H). – ^{13}C NMR ($CDCl_3$): δ = 47.10 (d), 49.80 (d), 51.21 (d), 64.95 (t), 128.82 (s), 216.99 (s). – MS (70 eV): *m/z* (%) = 257 (21), 256 (100) [M^+], 228 (23), 163 (30).

$C_{16}H_{16}O_3$ (256.3) Calcd. C 74.98 H 6.29
Found C 75.06 H 6.21

Heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane-7-one Ethylene Acetal (**1h**): A mixture of diethylene glycol (25 ml) and KOH (1.8 g, 28 mmol) in a round-bottom flask was heated until all of the solid KOH had dissolved. The temperature of the reaction flask then was adjusted to 80°C, and **1g** (720 mg, 2.8 mmol) was added. To the resulting mixture was added with stirring anhydrous hydrazine (1.0 g, 30 mmol), and the temperature of the reaction mixture was increased to 150°C. Stirring was then continued for 4 h. The reaction flask was fitted with a Dean-Stark apparatus, and the reaction temperature was increased to 200 – 210°C and was maintained at that temperature for ca. 12 h. The reaction mixture was then allowed to cool gradually to room temperature. Water (50 ml) was added, and the resulting mixture was extracted with Et_2O (3 × 50 ml). The combined extracts were washed with water (3 × 20 ml). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. Recrystallization of the residue thereby obtained from hexane afforded pure **1h** (510 mg, 75%) as a colorless microcrystalline solid, m. p. 76 – 77°C. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 1480, 1460, 1330, 1280, 1255, 1150. – ^{1}H-NMR ($CDCl_3$): δ = 1.85 – 1.91 (br. s, 2H), 2.17 – 2.23 (br. s, 2H), 2.32 – 2.36 (br. s, 2H), 2.47 – 2.60 (m, 8H), 3.88 – 3.93 (br. s, 4H). – ^{13}C NMR ($CDCl_3$): δ = 44.36 (t), 48.55 (d), 50.07 (d), 53.81 (d), 54.01 (d), 64.70 (t), 126.99 (s). – MS (70 eV): *m/z* (%) = 243 (22), 242 (100) [M^+], 170 (39), 163 (17).

$C_{16}H_{18}O_2$ (241.3) Calcd. C 79.20 H 7.67
Found C 79.30 H 7.49

Heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}0^{10,14}]tetradecane-7-one (**1b**): To a solution of **1h** (480 mg, 2.0 mmol) in CH_2Cl_2 (25 ml) at room temperature was added with stirring concentrated H_2SO_4 (96.7%, 1.0 g) and the resulting mixture was stirred for ca. 12 h. The reaction mixture was poured carefully into 5% aqueous $NaHCO_3$ solution (20 ml). The resulting mixture was extracted with Et_2O (2 × 50 ml), and the combined extracts were washed with water (2 × 10 ml). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. Compound **1b** (400 mg, 100%) was thereby obtained as a colorless microcrystalline solid, m. p. 200 – 201°C. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 1750, 1300, 1270, 1240, 1200, 1165. – ^{1}H-NMR ($CDCl_3$): δ = 2.03 – 2.07 (br. s, 2H), 2.27 – 2.35 (br. s, 4H), 2.48 – 2.54 (br. s, 4H), 2.68 – 2.75 (br. s, 4H). – ^{13}C-NMR ($CDCl_3$): δ = 46.23 (d), 46.38 (d), 46.68 (t), 53.41 (d), 55.97 (d), 217.97 (s). – MS (70 eV): *m/z* (%) = 199 (16), 198 (100) [M^+], 170 (49), 155 (23), 104 (46), 92 (43), 91 (38).

$C_{14}H_{14}O$ (198.3) Calcd. C 84.81 H 7.12
Found C 84.61 H 7.17

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