

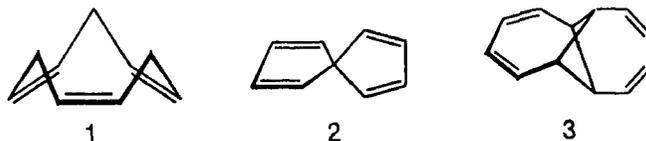
Interactions of π -systems via chains, rings and cages—syntheses of model compounds and their spectroscopic investigations

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Abstract: The interactions between two π -systems separated by chains, rings and cages are discussed. The focus is on systems with a bicyclo[3.3.0.0^{3,7}]octane skeleton (stellane) as building block. The syntheses of a number of model systems such as 2,6-stelladiene, 2,4,6-stellatriene and 2,2',6,6'-distellatriene are discussed. By means of He(I) photoelectron spectroscopy the interaction between the π -systems has been investigated. It is found that the stellane skeleton is a good relay.

The interaction between two π -systems can be classified into conjugation, homoconjugation, spiroconjugation and through bond interaction (1). If both π -systems are directly linked, as in 1,3-butadiene, we talk about conjugation. If the π -units are separated by one or a few sp^3 carbons they are still able to interact with each other mainly through space. Examples for such interactions are the homoconjugation in cyclononatriene (1) or the spiroconjugation in spirononatetraene (2). In 1968 it was recognized (2) that the interaction between



π -units can also be mediated by the σ -frame of a molecule (through bond interaction). On this subject several review articles have been published (3). In this paper we will focus on most recent achievements concerning the synthesis and properties of compounds with the tricyclo[3.3.0.0^{3,7}]octane unit (stellane) as building block.

Interaction via Rings

This research was stimulated by our theoretical (4) and spectroscopic investigations on tricyclo[5.5.0.0^{2,8}]dodecatetraene (3) and related species (5). It was shown that the four-membered ring in 3 acts as an excellent relay. A strong interaction between the central four-membered ring and the diene fragment is due to mainly two reasons: a) the basis orbital energies of the Walsh-type σ -MOs of the four-membered ring and the frontier π -MOs of the butadiene units are similar, b) there is a 1:1 matching between the π -MOs of the butadiene units and the Walsh-type MOs.

Similar conditions have been predicted in case of 2,6-dimethylene-tricyclo[3.3.0.0^{3,7}]octane (stelladiene) (4) and twistadiene (5). In Figure 1 we show the symmetry of the two occupied π -MOs and the two highest occupied π -MOs of 5.

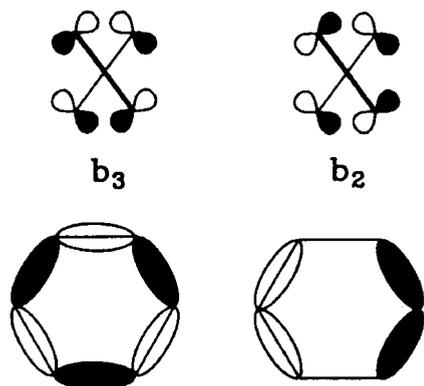
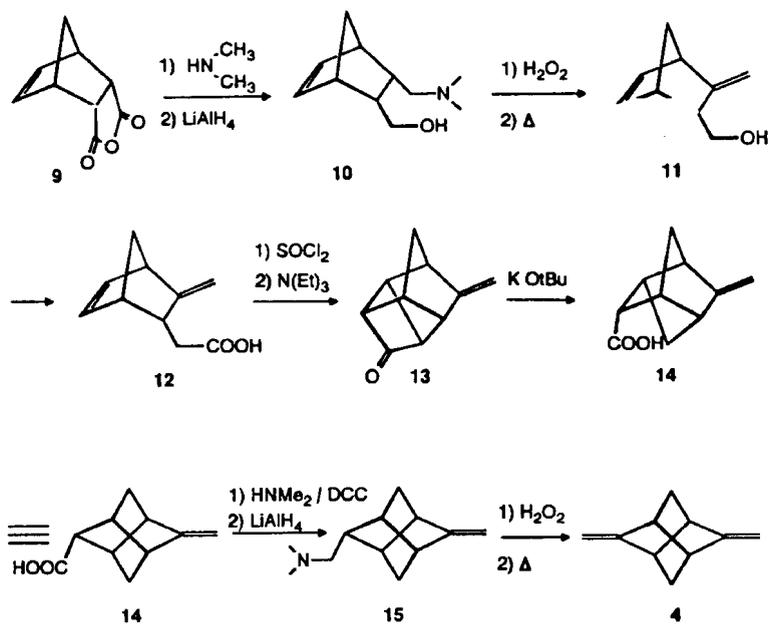


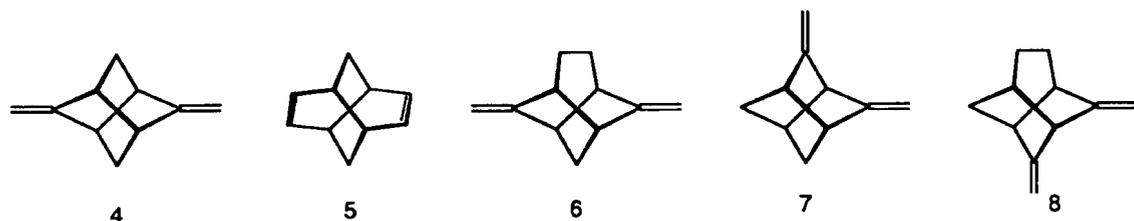
Fig. 1 Comparison between the symmetry of the two highest occupied π -MOs and σ -MOs of twistadiene.

To prepare **4** we followed a protocol shown in Scheme 1 (**6**). The first exomethylene group is introduced by a Cope elimination of the amine **10**. The tricyclic ring is formed by an intramolecular ketene addition to yield **13** and subsequent cyclobutanone ring opening. This sequence was first applied by Sauers *et al* (**7**).

Scheme 1



The method of choice to investigate the electronic structure of **4** is He(I) photoelectron (PE) spectroscopy. Together with **4** we also prepared **6** — **8** (**8**) and investigated the PE spectra of these species (**9**). The split of the first two bands in the PE spectra is given below the drawings. The sizeable splitting is due to a strong



$\Delta I (\pi)$ [eV] 0.9

1.3

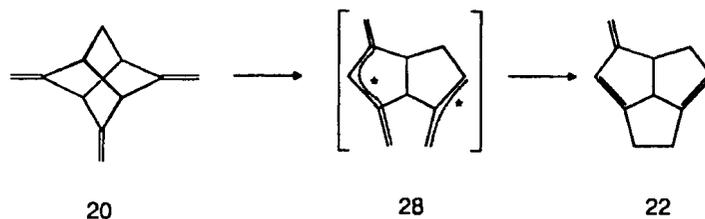
0.7

0.8

0.6

suggest that the Cope rearrangements of **19**, **20**, **23** and **24** occur via a stepwise mechanism as exemplified for **20** in Scheme 4. In a first step one of the central bonds breaks to yield the biradical **28** which finally collapses to **22**. This assumption would explain why the

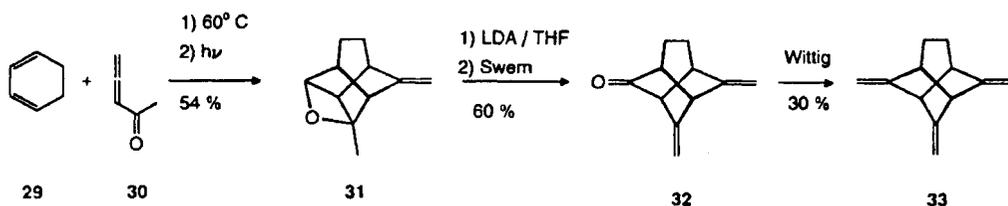
Scheme 4



terminal methyl groups contribute only to a minor extent to the stabilization of a stellatriene. Hence, stellatetraene should be less stable than **20** and it should be difficult to isolate at ambient temperature.

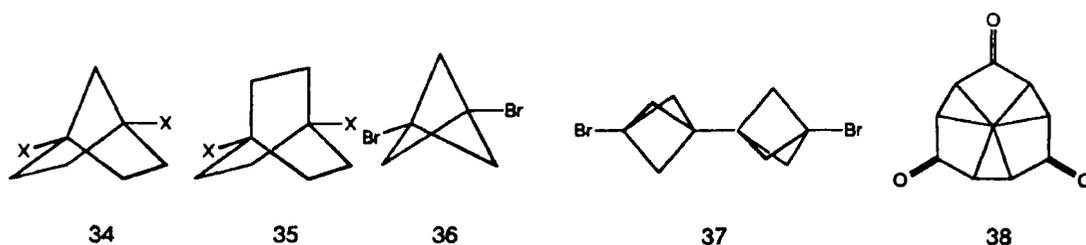
The synthesis of **33** (Scheme 5), a rather stable species, demonstrates that the stability increases when strain in the system is released (15). The PE investigation of **33** shows a strong through-space and through-bond interaction of the three double bonds (15).

Scheme 5



Interactions via Cages

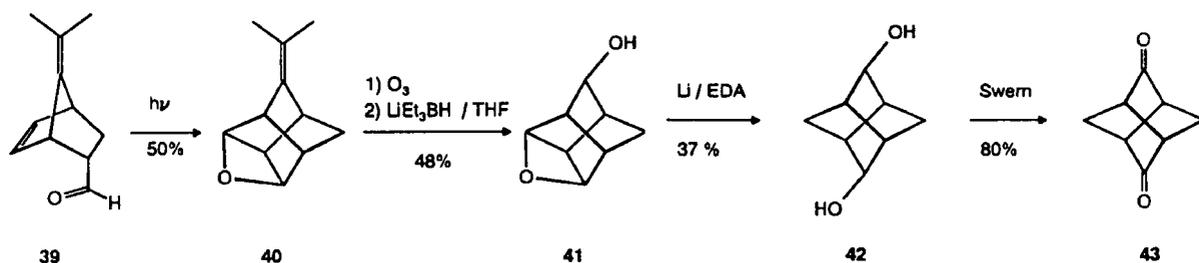
Similar to rings, cages might mediate the interaction between two π -systems or p-orbitals. Earlier investigations on bicyclo[2.2.2]octane- and bicyclo[2.2.1]heptane-derivatives (see below) show relative small splittings in their PE spectra (16). Much larger are the observed energy differences in the bicyclo[1.1.1]pentane species **36** and **37** (17) as well as in **38** (18).



$\Delta I_{1,2}$ [eV]	34	35	36	37	38
	0.3	0.2	0.7	0.4	0.8

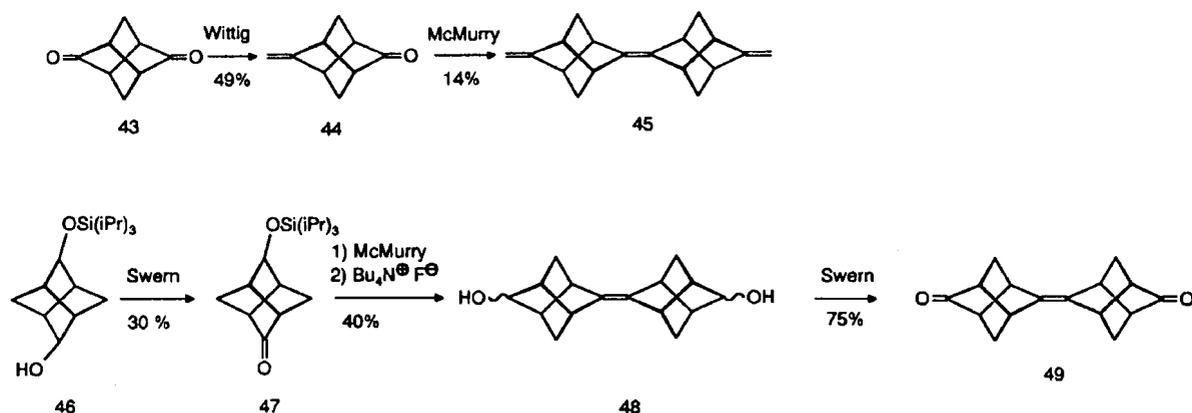
The strong π/σ -interaction in the case of **4** - **6** prompted us to probe the stellane skeleton as a relay. The simplest system to test this capability was the dione **43** which can be prepared in a straightforward way when the protocol given in Scheme 6 (19) is followed. The PE spectrum of **43** shows a 1 eV split between the bands belonging to the ionization process from n_+ and n_- . According to the MO calculations this split is due to a strong interaction of the central stellane σ -skeleton with the lone pairs which are 5.6 Å apart.

Scheme 6



The synthesis of **43** paved also the way to prepare the distellenes **45** and **49** (Scheme 7). In both cases three stereoisomers meso (C_{2h}) and racemic mixture (D_2) are possible. So far we have not been able to separate them.

Scheme 7



The relay properties of **45** and **49** have been investigated by means of PE spectroscopy supported by MO calculations. In the case of **49**, where both oxygens are 10.23 Å (MINDO/3) apart, the split between the lone-pair bands amounts to 0.28 eV. In case of **45** the energy difference between the ionization energies of the terminal π -bands amounts to 0.43 eV. Both values compare well with those derived from **37**.

Conclusion

Our investigations show that the σ -skeleton of a chain, ring or cage can interact strongly with an adjacent π -system. An analysis based on quantum chemical calculations shows that the σ -system of rings and cages meets the prerequisites for an efficient π/σ -interaction:

- a similar basis orbital energy of π - and σ -system
- the linear combinations of the π -MOs and the σ -MOs of the central unit belong to the same irreducible representation.

In view of the first point it is also understandable that a strained central unit such as a cyclobutane-, bicyclo[1.1.1]pentane- or stellane-skeleton with its high p-character of the C,C bonds should provide very efficient relays.

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