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Linear and Angular Interactions in Distellenes: Photoelectron Spectra and Ab Initio SCFMO Studies

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Abstract: The photoelectron spectra of *rac*-6,6′-diisopropylidene-2,2′-bis(tricyclo[3.3.0.0^{3,7}]octylidene) (**12**), *syn*- and *anti*-2,2′-bis(tricyclo[3.3.0.0^{3,7}]octane)-4,4′-dione (**13** and **14**), *syn*- and *anti*-4-methylidene-2,2′-bis(tricyclo[3.3.0.0^{3,7}]octylidene)-4′-one (**15** and **16**), and *anti*-4,4′-dimethylidene-2,2′-bis(tricyclo[3.3.0.0^{3,7}]-octylidene) (**18**) have been recorded. The energy difference between the 2p-type lone pairs of the angular oriented oxygen atoms of **13** and **14** amounts to 0.6 eV, while the corresponding energy difference in **4**, where the oxygen atoms are linearly orientated, is 0.2 eV. For **3** and **12,** in which the terminal π-bonds are arranged linearly, the difference between the first two peaks in their spectra is 0.4−0.5 eV, while the angular arrangement of the terminal π-bonds in **18** gives a splitting of only 0.2 eV. Hartree−Fock SCF calculations, using a 6-31G* basis set, have been used to interpret the photoelectron spectra of **12**−**16**, **18**, and **19**. The interactions between the σ frame and the n and π orbitals in these molecules have been investigated and analyzed in terms of the through-space through-bond concept. It is concluded that a maximum interaction between π bonds is attained, if they are arranged in a linear fashion, while the interaction between π bonds and keto groups reaches its maximum in an angular orientation.

Many investigations over the past years have shown that it is useful to subdivide the interactions of nonconjugated π-systems into those through space and those through bonds.[1] The through-space interaction of two π-moieties depends on their orientation with respect to each other and the distance between them. Of special interest are those cases in which the π-moieties are separated by one or two sp^3 centers (homoconjugation)[2] or where they are perpendicularly oriented (spiroconjugation).[3] The interaction of two π-moieties through an intervening σ-skeleton can take place through chains, rings, and cages.[4] By analyzing the photoelectron (PE) spectra of twistadiene (**1**) and *p*-stelladiene (**2**), it was possible to find cases in which a six-membered ring acts as a relay.[5] Continuing these studies we investigated the PE spectra of the distellenes **3** and **4**[6] and found a considerable splitting between the ionization energies assigned to the terminal π-bonds in **3** (0.43 eV), but only a small interaction between the 2p lone pairs on the oxygen atoms in **4** (0.11 eV).

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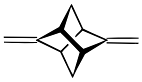

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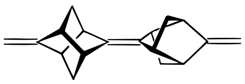

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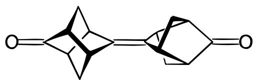

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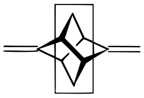
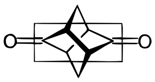
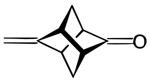
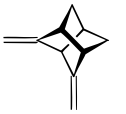
An analysis of the through-bond interactions found in **3** and **4** revealed that the terminal π bonds in **3** and the lone pairs on the carbonyl groups in **4** each interact via different relays.[6] To understand this led us first to examine the interactions in **2** and **5**−**9**.[7] In **2** the π orbitals of the terminal double bonds interact strongly with the orbitals of the central six-membered ring (indicated by the plane drawn in **2**). This results in a splitting of the first two ionization energies by 0.9 eV. By placing the *exo*-methylidene groups “*ortho*” to each other as in **7**, slightly

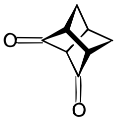


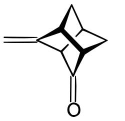




	2	**5**	**6**
$\Delta I_{v,j}$ [eV]	0.91	1.06	0.55







	7	**8**	**9**
$\Delta I_{v,j}$[eV]	0.84	0.80	1.12

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(1) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

(2) Reviews: Winstein, S. *Spec. Publ. Chem. Soc.* **1967**, *21*, 5. Warner, P. M. In *Topics in Nonbenzenoid Aromatic Chemistry*; Hirokawa Publishing Co.: Tokyo, 1977, Vol. 2283. Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 100.

(3) Simmons, H. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1967**, *89*, 5208; Hoffmann, R.; Imamura, A.; Zeiss, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5215. Review: Dürr, H.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 559.

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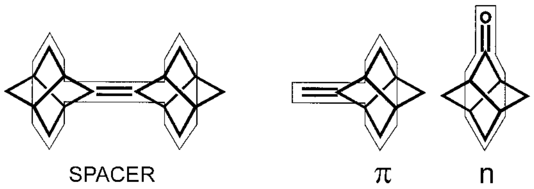


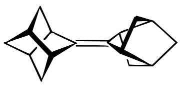
Figure 1. Building units for optimal interactions between *exo*-methylidene and keto groups (right) and central stellene unit.

less interaction is observed (0.84 eV). In the case of **5** the 2p lone pairs on the oxygen atoms of the CO groups interact strongly with the orbitals of the same six-membered ring, giving rise to a large splitting of 1.1 eV. However, as indicated by the plane drawn in **5**, the bonds of this six-membered ring are almost orthogonal to those through which the double bonds in **2** interact. In **8**, where the CO groups are situated "*ortho*" to each other, this interaction is reduced to 0.8 eV. In **6**, where one C−C π bond and one oxygen 2p lone pair is present, each interacts strongly with different bonds, so they do not have a common six-membered ring. The result is a reduced splitting (0.6 eV). This reduction cannot be solely due to the difference in energy between the C−C π and oxygen lone pair orbitals because, if *exo*-methylidene groups and CO groups are placed in the "*ortho*" position, the interaction between them is strong (1.1 eV in **9**). The splitting is large in **9** because the bonds of the same central six-membered ring act as a relay.

If we apply the outcome of this analysis to the distellene moiety, we expect strong interaction between both termini and the central π bond (i) if two terminal π bonds are connected linearly as in **3**, (ii) if two carbonyl groups are arranged angularly, and (iii) if a π and a carbonyl group are situated in, respectively, a linear and an angular fashion.

This is summarized in Figure 1, which indicates the bonds of the six-membered rings that interact with an *exo*-methylidene group, and the oxygen lone pair of a carbonyl group of a stellane unit (right) and the six-membered rings that interact with the central double bond of a distellene unit (left) are indicated. To obtain a maximum $\pi-\sigma-\pi-\sigma-\pi$, $\mathrm{n}-\sigma-\pi-\sigma-\mathrm{n}$, and $\mathrm{n}-\sigma-\pi-\sigma-\pi$ interaction, the six-membered rings in respective building blocks have to be aligned.

The $\pi-\pi$ interaction in **3** can be improved by raising the energy of the π orbitals of the terminal methylidene groups because their energy differs considerably from that of the central double bond. This can best be seen by comparing the first ionization energy of **10** (7.9 eV)[6] with that of **11** (9.0 eV).[6]



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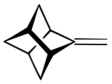

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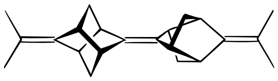
To raise the energies of the terminal π bonds we replaced the terminal methylidene groups of **3** by isopropylidenes. This leads us to synthesize *rac*-6,6′-diisopropylidene-2,2′-bis(tricyclo[3.3.0.0^{3,7}]octylidene) (**12**). To investigate the interactions of angularly oriented C−C π bonds and carbonyl oxygen lone pairs, we also prepared *syn*- and *anti*-2,2′-bis(tricyclo[3.3.0.0^{3,7}]octane)-4,4′-dione (**13** and **14**), *syn*- and *anti*-4-methylidene-2,2′-bis(tricyclo[3.3.0.0^{3,7}]octylidene)-4′-one (**15** and **16**), and *anti*-4,4′-dimethylidene-2,2′-bis(tricyclo[3.3.0.0^{3,7}]octylidene) (**18**).[8] In this paper we report the photoelectron spectra of **12**−**16** and **18**.



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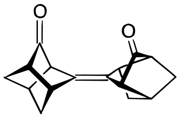

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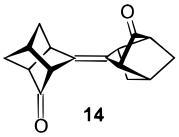

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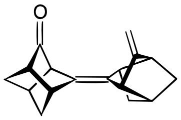

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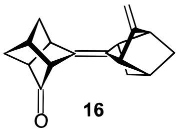

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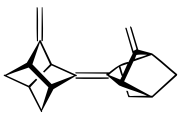

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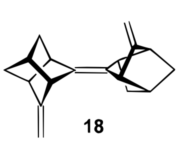

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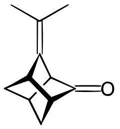

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Results

The syntheses of **12**−**16** and **18** have recently been reported.[8] The stereochemical possibilities of the distellanes can be illustrated for endiones **13** and **14**. Both can formally be viewed as being derived by olefin metathesis of two *ortho*-stellenones **9**. Since this molecule is chiral, the *syn* and *anti* metathesis products can each give rise to three possible stereoisomers—the two enantiomers of a C_2 symmetric racemate and an achiral *meso* compound with C_s symmetry in the *syn* stereoisomer and C_i in the *anti*. Of the total of four possible diastereomers, only the *rac*-C_2-*syn* (**13**) and the *rac*-C_2-*anti* (**14**) endiones could be obtained experimentally. [Using the terms *syn*/*anti* for the C_2-symmetric racemates is a little arbitrary because the keto groups are not situated in a common plane but have dihedral angles of ca. 120° (C_2-*anti*) and 50° (C_2-*syn*), whereas for the *meso* compounds, the dihedral angles are exactly 0° (C_s-*syn*) and 180° (C_i-*anti*).] The same stereochemical possibilities exist for the trienes **12**, **17**, and **18** as well as for the dienones **15** and **16**.

An X-ray investigation of *rac*-**12** revealed a distance of 10.33 Å between the terminal sp^2 centers of the isopropylidene groups.[8] The two isopropylidene groups in this stereoisomers are not coplanar. In fact, the two independent molecules in the unit cell have dihedral angles between the isopropylidene groups of 74° and 83°. For **13** the distance between the oxygen atoms was found to be 5.03 Å with a dihedral angle between the CO groups of 53°.[8] For **14** the distance between the oxygen atoms was found to be 6.55 Å with a dihedral angle between the CO groups of 118.5°.[8]

PE Spectra. The PE spectra of **12**−**16** and **18** are shown in Figures 2 and 3, and the measured vertical ionization energies are summarized in Table 1.

The PE spectrum of **12** shows four, clearly separated peaks below 10 eV. Similarly four separate peaks can be found below 11 eV in the PE spectra of **13** and **14** (Figure 2). In the cases

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[8] Gleiter, R.; Fritzsche, G.; Borzyk, O.; Oeser, T.; Rominger, F.; Irngartinger, H. *J. Org. Chem.* **1998**, *63*, 2878.

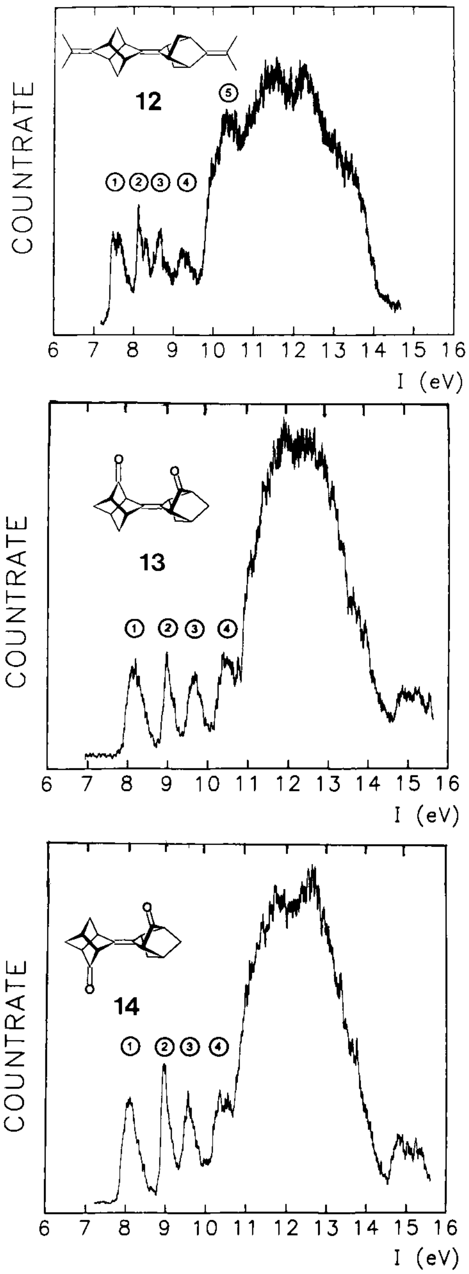

Figure 2. Photoelectron spectra of **12**−**14**.

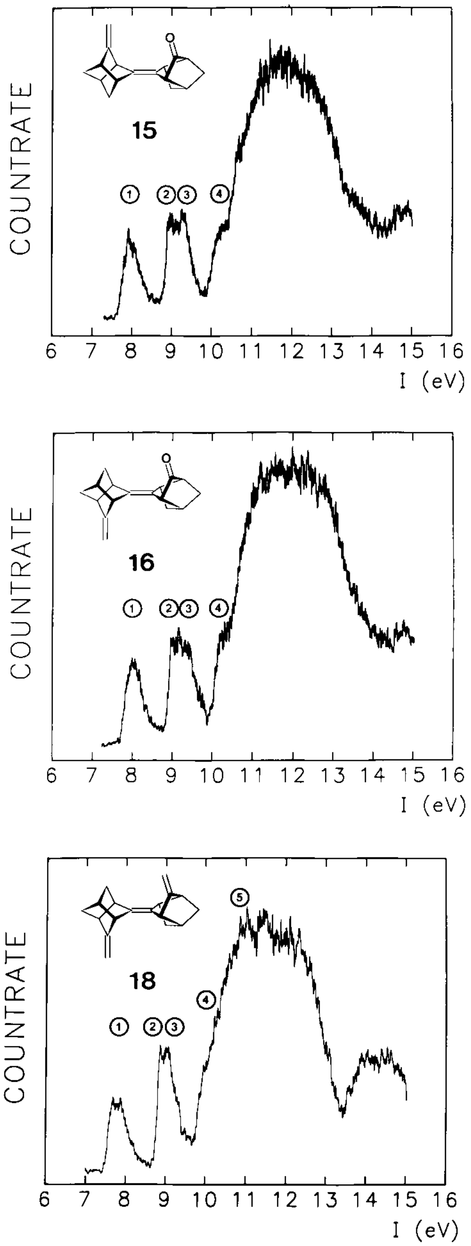

Figure 3. Photoelectron spectra of **15**, **16,** and **18**.

of **15**, **16**, and **18** the spectra exhibit fewer distinct peaks at low energy. The first peak is followed by a second, which shows a larger area below the band envelope. Therefore we assigned two ionization events to this second peak. To assign the bands to individual transitions we use Koopmans' theorem.[9] This allows the vertical ionization energies to be correlated with the calculated molecular orbital energies.

In Figure 4 we have correlated the first bands in the PE spectrum of **19** (π, n) with those of **4** and **13**−**16**. This correlation suggests attributing the low-energy band around 8 eV to an ionization from the π-orbital of the central π-bond. This comparison suggests assigning the second and third band, which lie close to each other in the PE spectra of **15** and **16,** to ionizations from π- and n-orbitals, respectively. On the basis of this correlation the assignment of the first bands in the PE spectra of **13** and **14** becomes straightforward. It leads to the sequence $\pi < n < n$ and shows a relative strong splitting (0.60−0.67 eV) between the second and third bands. This splitting is considerably larger than that observed in the PE spectrum of **4**.

In Figure 5 we compared the first PE bands of **12** and **18** with those of **3** and **10**. This suggests attributing the first band in the PE spectra of **12** and **18** to the ionization from the central double bond. Bands 2 and 3 in the PE spectra of **12** and **18** are due to the ionization of the π-MOs localized mainly at the terminal double bonds. As anticipated from the preceding discussion, the splitting of bands 2 and 3 is large in the PE spectra of **3** and **12** but small in the spectrum of **18**.

Computations

Methodology. The geometries of molecules **12** (D_2), **13** (C_2), *meso*-**13** (C_s), **14** (C_2), **15** (C_1), **16** (C_1), **17** (C_2), **18** (C_2), and **19** (C_1) were optimized at the Hartree−Fock level of theory using the 6-31G* basis set.[10] Where possible, we made use of symmetry restrictions. We use Koopmans' theorem[9] to assign the HF-SCF orbital energies ($-\epsilon_j$) to the ionization events.

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[9] Koopmans, T. *Physica* **1934**, *1*, 104.

[10] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

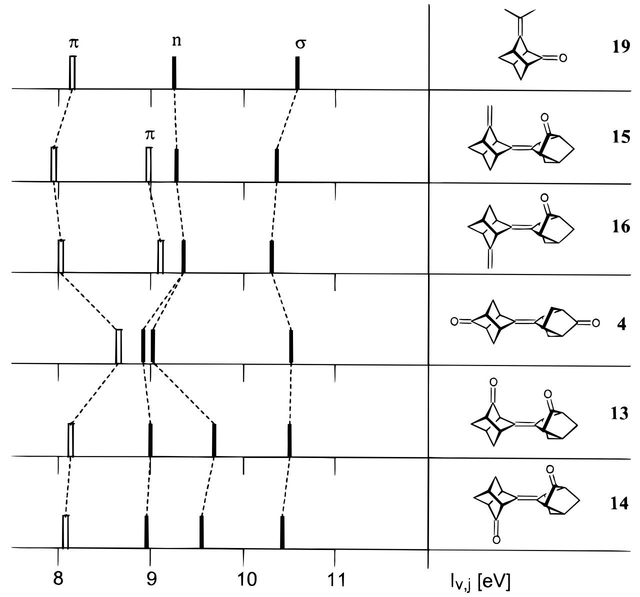

Figure 4. Correlation between the first ionization energies of **4**, **13**−**16,** and **19**.

Table 1. Comparison between Vertical Ionization Energies, $I_{v,j}$, of **12**−**16**, **18**, and **19** with the Calculated ($-\epsilon_j$, RHF/6-31G*) Energies (All Values in eV)

compd	band	$I_{v,j}$	assignment	$-\epsilon_j$
12	1	7.6	$19b_2$, π	8.10
	2	8.2	$18b_1$, π	8.68
	3	8.7	$18b_2$, π	9.28
	4	9.3	$17b_2$, σ	10.44
	5	10.3	$17b_1$, σ	11.34
13	1	8.1	33a, π	8.92
	2	9.0	31b, n	10.39
	3	9.6	32a, n	10.84
	4	10.5	31a, σ	11.74
14	1	8.1	32b, π	8.95
	2	9.0	32a, n	10.44
	3	9.6	31b, n	10.85
	4	10.4	30b, σ	11.75
15	1	8.0	64a, π	8.53
	2	9.0	63a, π	9.59
	3	9.3	62a, n	10.42
	4	10.3	61a, σ	11.37
16	1	8.0	64a, π	8.57
	2	9.1	63a, π	9.65
	3	9.3	62a, n	10.44
	4	10.3	61a, σ	11.39
18	1	7.8	32b, π	8.21
	2	8.8	32a, π	9.38
	3	9.0	31b, π	9.54
	4	10.0	30b, σ	11.13
19	1	8.1	44a π	8.87
	2	9.2	43a, n	10.49
	3	10.6	42a, σ	11.85

The electronic structures of the molecules were further investigated in terms of the through-space (TS)/through-bond (TB) concept developed by Hoffmann.[1] We make use of a methodology first suggested by Heilbronner and Schmelzer[11] which is based on the Fock matrix in a localized basis. For a qualitative treatment we apply the procedure of Imamura et al.,[12] using Weinhold's natural bond orbitals[13] (NBOs) as a starting point.[14] The calculations were performed using the Gaussian94 program.[15]

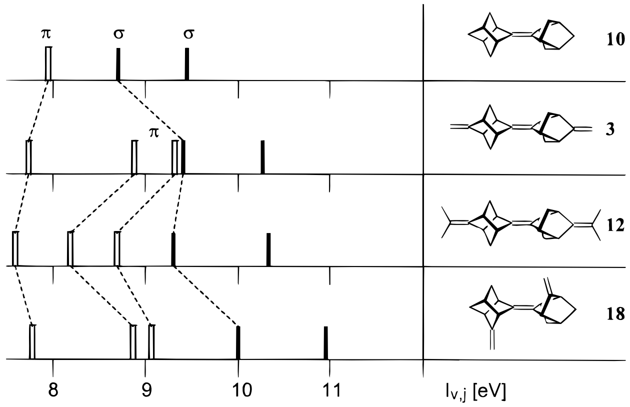

Figure 5. Correlation between the first ionization energies of **3**, **10**, **12,** and **18**.

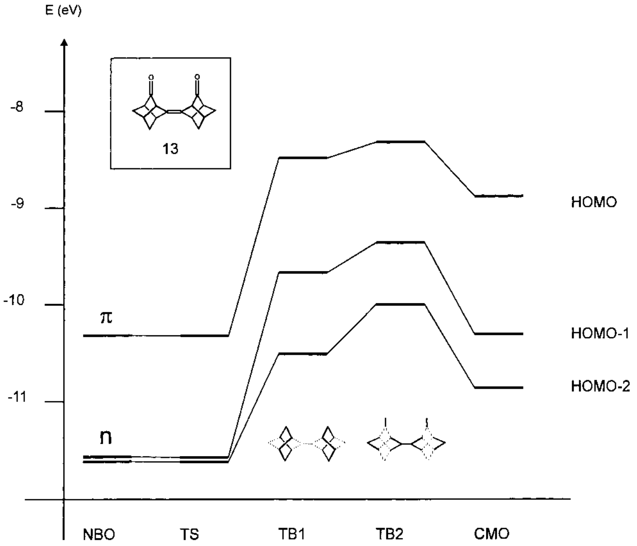

Figure 6. TS/TB interaction diagram of **13**. NBO: localized orbitals. TS: orbitals after through-space interaction. TB1: orbitals after interaction with the ribbon orbitals (indicated in black). TB2: orbitals after interaction with the remaining σ orbitals. CMO: canonical molecular orbitals. For the sake of clarity we represent the molecules in their meso configuration.

Enediones 13 and 14. As can be seen in Table 1 and Figure 4, the ionization energies of both compounds are almost identical. In other words, the n−n interaction between the lone pairs on the oxygens does not depend on the relative orientation of the two carbonyl groups and must therefore be exclusively of the through-bond type. The absence of any through-space interaction can also be concluded from inspection of the interaction diagram for the *rac*-C_2-*syn* endione **13** in Figure 6 (TS = through space in Figure 6). The same effect can be observed in the *meso*-C_s-*syn* isomer, the best candidate for a possible through-space interaction, since the keto groups are coplanar.

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[11] Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936.

[12] Imamura, A.; Ohsaku, M. *Tetrahedron* **1981**, *37*, 2191.

[13] Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys* **1985**, *83*, 735. Reed, A. E.; Weinhold, F. *Ibid.* **1983**, *78*, 4066.

[14] Liang, C.; Newton, M. D. *J. Phys. Chem.* **1992**, *96*, 2855. Naleway, C. A.; Curtiss, L. A.; Miller, J. R. *Ibid.* **1991**, *95*, 8434. Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Am. Chem. Soc.* **1990**, *112*, 1710.

[15] We used Gaussian 94 program by: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; A Montgomery, J.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanyakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen. W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1995.

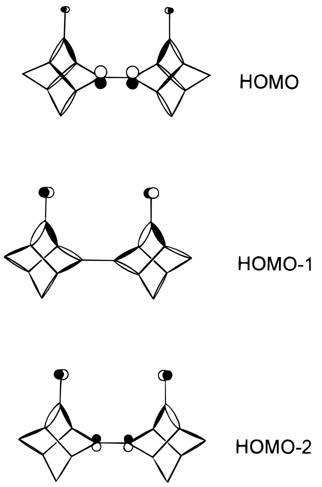

Figure 7. Schematical drawing of the four highest occupied orbitals of **13**. For the sake of clarity we represent the molecules in their meso configuration.

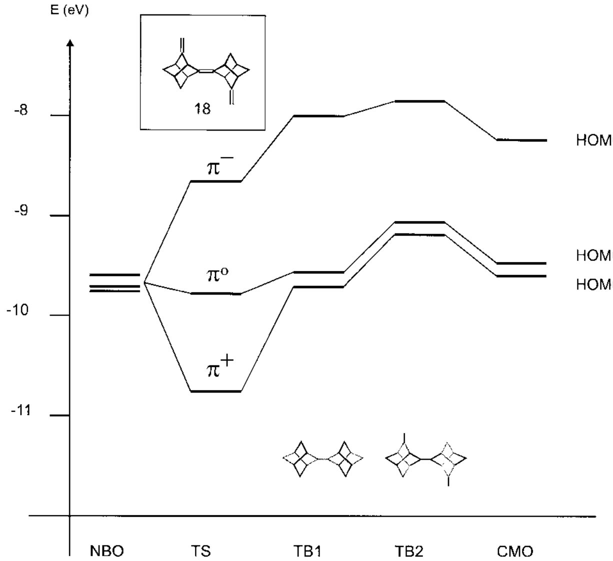

Figure 8. TS/TB interaction diagram of **18**. For the meaning of NBO, TS, TB1, TB2, and CMO see legend of Figure 6.

As expected, the n−n splitting in **13** (exptl 0.67 eV, calcd 0.45 eV) as well as in **14** (exptl 0.60 eV, calcd 0.41 eV) is larger than in the linear counterpart (exptl 0.11, calcd 0.35). The essential effect can be seen in the TB1 step of the diagram. Here, the interaction of the functional groups is enforced by the ribbon orbitals of the two stellane fragments. The resulting splitting (calcd 0.81 eV) is much stronger than in the linear isomer **4** (calcd 0.12 eV). The following TB2 and CMO steps only lead to an overall shift of the orbital energies but not to a significant relative change. The HOMO of **13** reveals high π character (48%), compared to the n orbitals (14%), whereas only lone pair participation can be observed in the HOMO-1 (46%). The HOMO-2 contains about the same amount of π-character (30%) and n-character (25%) (Figure 7).

Trienes 12 and 18. In addition to the *rac*-C_2-*anti* isomer **18** our calculations also included *rac*-C_2-*syn* **17**. First we focus on the angular compounds. The most striking difference from the diones is the large through-space interaction of the two exocyclic double bonds and the central one (Figure 8). This might have been anticipated from the analogous interaction in *o*-stelladiene **7** which was calculated to be 1.41 eV. However, there is no direct *exo*−*exo* interaction in the case of **18** and only a very small one between the π units in **17** (0.12 eV). The TS step leads to three nearly equidistant linear combinations in **18**, π^+ at 10.69 eV, π^0 at 9.73 eV, and π^- at 8.60 eV (Figure 8). Taking the ribbon orbitals into consideration, one observes a strong destabilizing interaction of the low-lying π^+, a smaller one for the π^0, and again a strong one for the π^- orbital. The explanation for this is obvious: The π^+ and π^- orbitals both have large coefficients at the central double bond and interact therefore very well with the ribbon orbitals. In contrast, π^0 is, for symmetry reasons, a linear combination of only the *exo* double bonds that are not able to interact significantly through the unfavorably oriented twist cyclohexane rings. As a result, π^0 and π^+ are now energetically close, well separated from the π^- orbital. This is exactly the splitting found in the PE spectrum of **18**. The splitting of the *exo* π bonds is very small (**18**: exptl 0.19 eV, calcd 0.26 eV) and, again, nearly independent of the relative orientation of the *exo* bonds (**17**: calcd 0.23).

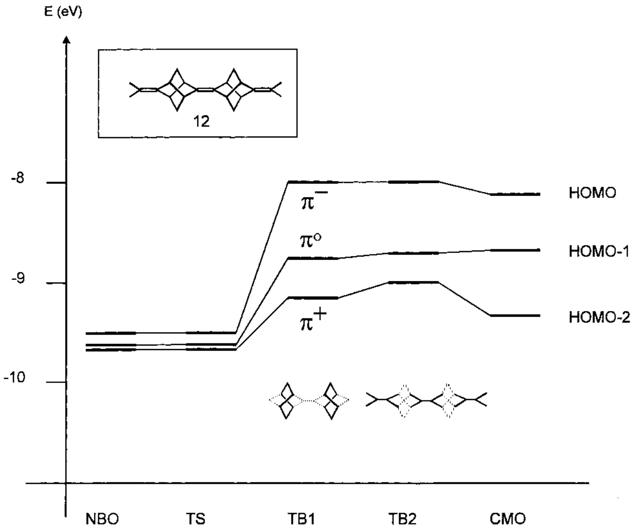

Figure 9. TS/TB interaction diagram of **12**. For the meaning of NBO, TS, TB1, TB2, and CMO see legend of Figure 6.

The interactions in the linear D_2 symmetric triene **12** are completely different from those in **18** and resemble more the interactions in the angular diketones **13** and **14**. In **12** the large distance between the terminal π-bonds, together with the unfavorable orientation of the functional groups (the π planes are twisted about 70−80°) prevents the through-space interaction, between both *exo* bonds as well as between the *exo* and the *endo* bonds (TS in Figure 9). The π orbitals do not "notice" each other until the ribbon orbitals of the two stellane units are introduced. This finally generates three nearly equally separated CMOs, which are well separated from the σ orbitals. This σ−π separation was not present in the triene **3**, where the bands 2−4 strongly overlapped.[6] Our analysis shows that both the inductive (+I) and the hyperconjugative (+H) effects of the methyl groups contribute each a shift of about 0.3 eV to the neighboring π orbitals, but only about 0.1 eV (+I) to the σ orbital.

The long-range π interaction in **12**, which results in splittings of 0.5 eV, is remarkable. The bonds of the stellane cage acts as a very efficient mediator of the π−π conjugation. Thus, the extension of the spacer to three or four stellane units seems to be a theoretically interesting synthetic goal.

Dienones 15 and 16. By comparing the interaction diagrams for the mixed compounds with those for **13** or **14**, one observes a behavior that could have been anticipated from the preceding discussion. First, the TS splitting of the π bonds is analogous to the coupling in *o*-stelladiene **7**, whereas the lone pair remains

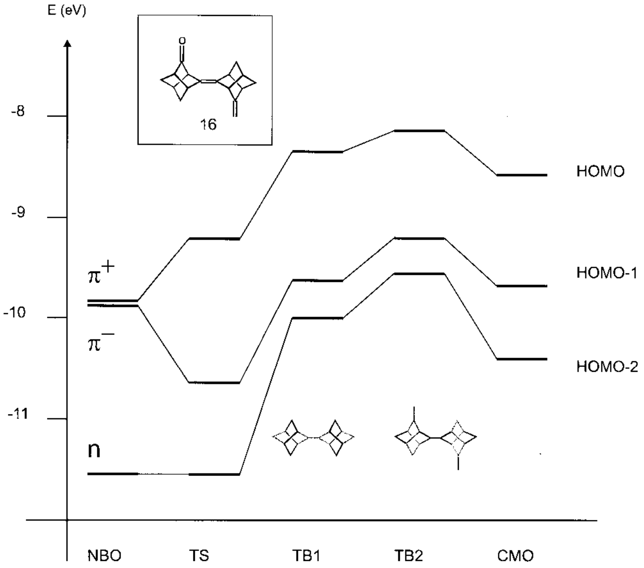

Figure 10. TS/TB interaction diagram of **16**. For the meaning of NBO, TS, TB1, TB2, and CMO see legend of Figure 6.

uninfluenced. Second, the ribbon orbitals interact with the π^+ and π^- orbitals, but mix most effectively with the low-lying n orbital, which is raised in energy sufficiently, that it lies close to the π^+ combination in energy (Figure 10). The resulting π−n splitting of **15** and **16** is therefore small (0.2−0.3 eV). The poor agreement between calculation and experiment with respect to the π−n splitting in the case of **15** and **16** needs an additional comment. As has been shown earlier,[6] strong Koopmans' defects can be observed with stellane derivatives containing both C−C π bonds and carbonyl groups. This is due to the greater electronic relaxation of the states resulting from oxygen lone pair ionization than from ionization of π orbitals.

Conclusion

The simple interaction concept that provides an understanding of the coupling of two functional groups in the monomeric stellanes can successfully be applied to the distellanes. The major difference, both predicted and found, between the angular and linear isomers can be traced back to the mediating ability of the spacer unit. The spacer provides the most effective coupling if π bonds are arranged in a linear fashion and if keto groups are arranged in an angular fashion. One can use the stellane fragments as building blocks to design molecules whose geometries confer on them the desired electronic properties, and compounds with unfavorable geometries can easily be ruled out.

Experimental Section

The preparation of **12**−**16** and **18** has recently been described.[8] The He I PE spectra were recorded on a Perkin-Elmer PS18 spectrometer. The recording temperatures were as follows: **12**, 80 °C; **13** and **14**, 130 °C; **15**, 90 °C; **16**, 75 °C; **18**, 60 °C. The calibration was performed with Ar (13.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of 20 meV on the $P_{3/2}$ Ar line was obtained.

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