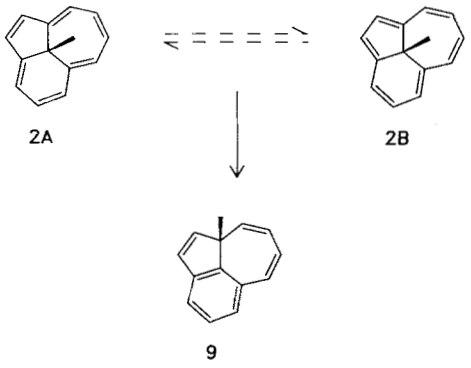
trum, which is temperature-independent up to 80°C, the structure of the π-bond isomer **2A** could be deduced on the basis of the coupling constant $J = 5.8$ Hz for the AB system of 1 H and 2 H and the vicinal coupling constants of 3-H, 5-H, 6-H, and 9-H. In comparison to the spectrum of the dihydro derivative **8**, in the spectrum of **2** the signals of the central methyl group and of the peripheral ring protons appear in the opposite sequence. The signals of the perimeter protons exhibit a strong upfield shift of about 2 ppm in the range $\delta = 3.88$–**4.69**, whereas the methyl group singlet experiences a substantial downfield shift of about 4 ppm to $\delta = 4.75$. The extremely high-field resonances of the ring protons of **2** compared to the ^{1}H-NMR shifts of the perimeter protons of [12]annulene ($\delta = 5.91$), 1,7-methano[12]annulene ($\delta = 5.1$–5.8) and 1,6-methano[12]annulene ($\delta = 5.50$–6.17) are consistent with a pronounced paramagnetic ring current in the 12π-perimeter of **2**.

The electronic spectrum of **2** (see Table 1), like those of the mono- and bicyclic [12]annulenes and the dehydro[12]annulenes,[14] shows a strong absorption in the region of 260 nm and, in contrast to these, an additional long-wave absorption at 567 nm. The absorption corresponds to the singlet-electron transitions calculated by *Lindner*[15a] for the localized 12π-electron system **2A**.



According to π-SCF force field calculations,[15b] the standard enthalpies of formation of **2A** and **2B** should be about the same, and the activation enthalpies for the π-bond shift should be more than 25 kcal·mol^{-1}. However, contrary to expectations based on these calculations, isomer **2B** was not detected. Hence, the equilibrium may lie further to the side of **2A** than predicted by the calculations, or a higher barrier between **2A** and **2B** is involved. At elevated temperatures a, presumably sigmatropic, methyl-group shift takes place in **2** — as is found in the case of **1**;[5] the 9a-methyl-9a*H*-benz[*cd*]azulene **9** (yellow oil) having a benzenoid partial structure is formed. In contrast to **1**, this isomerization already occurs at 80°C (in dimethyl sulfoxide) in case of **2**, and proceeds quantitatively within 15 min in boiling xylene.

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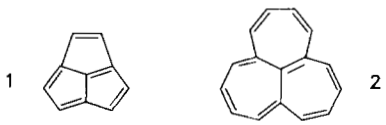
CAS Registry numbers:
7, 101998-44-1; **8**, 101998-45-2; **2**, 101998-46-3; **9**, 101998-47-4.

[1] E. Vogel, H. Königshofen, K. Müllen, J. F. M. Oth, *Angew. Chem. 86* (1974) 229; *Angew. Chem. Int. Ed. Engl. 13* (1974) 281.
[2] J. F. M. Oth, H. Röttele, G. Schröder, *Tetrahedron Lett. 1970*, 61; J. F. M. Oth, J.-M. Gilles, G. Schröder, *ibid. 1970*, 67.
[3] E. Vogel, M. Mann, Y. Sakata, K. Müllen, J. F. M. Oth, *Angew. Chem. 86* (1974) 231; *Angew. Chem. Int. Ed. Engl. 13* (1974) 283.
[4] D. Farquhar, T. T. Gough, D. Leaver, *J. Chem. Soc. Perkin Trans. 1 1976*, 341, and references cited therein; W. Flitsch, A. Gurke, B. Müter, *Chem. Ber. 108* (1975) 2969.
[5] R. McCague, C. J. Moody, C. W. Rees, *J. Chem. Soc. Perkin Trans. 1 1984*, 165 and following publications.
[6] Attempts to synthesize 9b-Methyl-9b*H*-phenalene have been reported by M. Moore, A. Amaro, P. D. Noire, K. G. Grohmann, *Abstr. 4. Int. Symp. Chem. Novel Aromatic Compounds*, Jerusalem 1981.
[7] K. Müllen, *Pure Appl. Chem. 58* (1986) 177.
[8] K. Hafner, H. Pelster, H. Patzelt, *Justus Liebigs Ann. Chem. 650* (1961) 80; K. Hafner, *Pure Appl. Chem. 28* (1971) 153; K. Hafner, K.-P. Meinhardt, W. Richarz, *Angew. Chem. 86* (1974) 235; *Angew. Chem. Int. Ed. Engl. 13* (1974) 204.
[9] V. Kühn, K. Hafner, unpublished.
[10] N. Kornblum, *Angew. Chem. 87* (1975) 797; *Angew. Chem. Int. Ed. Engl. 14* (1975) 734.
[11] W. Treibs, H. Froitzheim, *Justus Liebigs Ann. Chem. 564* (1949) 43; R. N. McDonald, N. L. Wolfe, H. E. Petty, *J. Org. Chem. 38* (1973) 1106; M. Müller, *Dissertation*, Technische Hochschule Darmstadt 1982.
[12] Correct elemental analyses or mass spectra were obtained for all the compounds described.
[13] We thank Dr. *S. Braun* for recording and discussing a 2D-^{1}H-NMR spectrum (COSY) of **2**.
[14] K. G. Untch, D. C. Wysocki, *J. Am. Chem. Soc. 88* (1966) 2608; F. Sondheimer, R. Wolovsky, P. J. Garratt, I. C. Calder, *ibid. 88* (1966) 2610.
[15] a) H. J. Lindner: Singlet transitions of **2A** calculated according to the π-SCF-CI method: λ_{max}(oscillator strength) = 244 (1.873), 255 (0.941), 297 (0.003), 580 nm (0.005); b) H. J. Lindner, *Tetrahedron 30* (1974) 1127; Program PIMM 82, unpublished, Technische Hochschule Darmstadt 1982.

Synthesis and Dynamic Properties of Substituted Cyclohepta[*ef*]heptalene**

By *Klaus Hafner,* Günter L. Knaup,* and *Hans Jörg Lindner*

As in the case of the mono- and bicyclic [4n]-π-electron systems cyclobutadiene,[1a] cyclooctatetraene,[1b] pentalene[1c] and heptalene,[1d] which contain localized double bonds in the ground state, a π-bond shift should also be observed in polycyclic non-alternating [4n]-π-electron systems. However, all previously reported *peri*-annelated tri- and tetracyclic compounds[2] with [4n]-π-electrons contain either benzenoid or azulenoid partial structures, which impede this dynamic process. The still unknown tricycles cyclopenta[*cd*]pentalene **1** and cyclohepta[*ef*]heptalene **2**,[3,4] on the other hand, do not have any aromatic structural elements. In contrast to the mono- and bicyclic [4n]-π-systems, in the case of **1** and **2** three isodynamic structures with localized double bonds should be in equilibrium with each other. Furthermore, the seven-membered rings of cyclohepta[*ef*]heptalene (pleiaheptalene) **2** should prefer a boat conformation, so that a ring inversion also could occur as a further dynamic process in this tricycle, as in the case of cyclooctatetraene[1b] and heptalene.[5] With the synthesis of substituted cyclohepta[*ef*]heptalenes we have now



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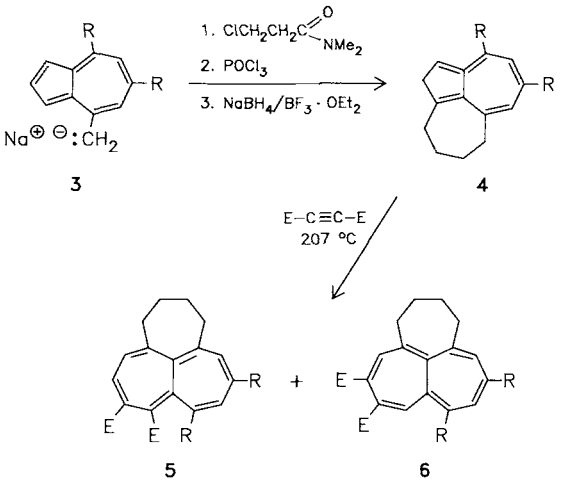
succeeded for the first time in investigating the dynamic processes of a tricyclic 16π-electron system.

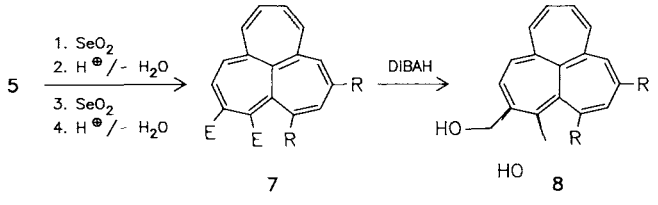
Alkylation of the sodium 4-methyleneazulenides **3a** and **3b**[6] with 3-chloropropionic acid *N,N*-dimethylamide (tetrahydrofuran (THF), −70°C), subsequent intramolecular Vilsmeier reaction with phosphoryl chloride (THF, 67°C) and reduction of the keto group with $NaBH_4/BF_3 \cdot OEt_2$ (1,2-dimethoxyethane, 0°C) afforded the tetrahydroace-



3 4 5 6

a: R = H; b: R = Me; E = CO_2Me

heptylenes **4a**[7] (blue platelets, m.p. 66°C; yield 39%) and **4b** (blue crystals, m.p. 52°C; yield 40%), respectively, whose reactions with dimethyl acetylenedicarboxylate (tetralin, 207°C) lead to the heptalene derivatives **5a** (yellow platelets; m.p. 128–129°C; yield 35%) and **6a** (yellow crystals, m.p. 133°C; yield 53%) as well as **5b** (yellow rhombs, m.p. 158°C; yield 23%) and **6b** (yellow crystals, m.p. 135°C; yield 1%), respectively. Since dehydrogenation of **5a** and **5b** with chloroanil or 2,3-dicyano-5,6-dichloro-*p*-benzoquinone proved unsuccessful, the missing double bonds were successively introduced by oxidation with selenium dioxide (dioxane, 90°C) to give the hydroxy compounds and subsequent elimination of water (TosOH/C_6H_6/80°C).[8] The completely unsaturated tricycles **7a** (orange-red platelets, m.p. 173–175°C; yield 18%) and **7b** (red crystals, m.p. 147–148°C; yield 7%) are stable towards heat and atmospheric oxygen.



7 8

a: R = H; b: R = Me; E = CO_2Me

As shown by the result of the X-ray structure analysis[9] of **7a** (Fig. 1), the achiral tricycle **2** has C_s symmetry and alternating bond lengths. Due to the puckering of the seven-membered rings, the molecule adopts a saddle shaped conformation.

Table 1. Spectral data of compounds **4–8**. ^{1}H-NMR (300 MHz): **4a**, **4b**, **5a**, **5b**, **6a**, **6b** in $CDCl_3$, **7aA**, **7bA**, **8bA**, **8bB** in [D_6]DMSO; UV: **4a**, **4b**, **5a**, **6a** in *n*-hexane, **5b**, **6b**, **7aA**, **7bA**, **8bA** in dioxane.

4a: ^{1}H-NMR: δ = 1.98–2.20 (m; 4H, 4,4′,5,5′-H), 3.26 (m; 4H, 3,3′,6,6′-H), 6.81 (dd, *J* = 10.2, 9.5 Hz; 1H, 9-H), 6.82 (d, *J* = 10.1 Hz; 1H, 7-H), 7.16–7.22 (br. s; 1H, 1-H), 7.26 (td, *J* = 10.1, 1.0 Hz; 1H, 8-H), 7.56 (br. s; 1H, 2-H), 8.09 (dd, *J* = 9.5, 1.3 Hz; 1H, 10-H); UV: λ_{max} (lgε) = 245 (4.30), 269 sh (4.27), 274 sh (4.47), 279 sh (4.58), 283 (4.66), 288 sh (4.64), 293 sh (4.45), 302 (4.02), 322 sh (3.25), 327 sh (3.36), 335 (3.53), 347 sh (3.64), 350 (3.70), 363 (3.22), 393 sh (1.18), 502 sh (1.94), 520 sh (2.14), 540 sh (2.30), 563 sh (2.44), 582 (2.52), 604 (2.60), 631 (2.54), 660 (2.56), 693 (2.22), 732 (2.19) nm

4b: ^{1}H-NMR: δ = 1.94–2.14 (m; 4H, 4,4′,5,5′-H), 2.51 (s; 3H, 10-Me), 2.76 (s; 3H, 8-Me), 3.21 (m; 4H, 3,3′,6,6′-H), 6.77, 6.80 (2s; each 1H, 7,9-H), 7.18 (d, *J* = 3.8 Hz; 1H, 1-H), 7.38 (d, *J* = 3.8 Hz; 1H, 2-H); UV: λ_{max} (lgε) = 216 (4.09), 247 (4.40), 290 (4.69), 295 (4.67), 307 sh (4.08), 327 sh (3.33), 341 (3.57), 351 sh (3.62), 357 (3.71), 368 sh (3.00), 522 sh (2.37), 545 sh (2.52), 567 sh (2.61), 582 (2.65), 603 (2.61), 631 (2.58), 663 sh (2.30), 695 (2.14) nm

5a: ^{1}H-NMR: δ = 1.10–2.78 (m; 8H, $-(CH_2)_4-$), 3.66, 3.70 (2s; each 3H, $2CO_2Me$), 6.07 (dm, *J* = 10.6 Hz; 1H, 12-H), 6.29 (d, *J* = 5.8 Hz; 1H, 4-H), 6.30 (ddd, *J* = 10.6, 5.6, 1.5 Hz; 1H, 11-H), 6.47 (ddd, *J* = 11.3, 5.6, 0.8 Hz; 1H, 10-H), 6.54 (dm, *J* = 11.3 Hz; 1H, 9-H), 7.48 (d, *J* = 5.8 Hz; 1H, 3-H); UV: λ_{max} (lgε) = 214 (4.35), 272 (4.32), 329 (3.56) nm

5b: ^{1}H-NMR: δ = 1.11–2.70 (m; 8H, $-(CH_2)_4-$), 1.95 (d, *J* = 1.2 Hz; 3H, 12-Me), 2.04 (d, *J* = 1.2 Hz; 3H, 10-Me), 3.69, 3.70 (2s; each 3H, $2CO_2Me$), 5.99 (quint, *J* = 0.9 Hz; 1H, 11-H), 6.13 (br. s; 1H, 9-H), 6.30 (d, *J* = 6.1 Hz; 1H, 4-H), 7.52 (d, *J* = 6.1 Hz; 1H, 3-H); UV: λ_{max} (lgε) = 274 (4.24), 324 sh (3.56), 386 sh (2.91) nm

6a: ^{1}H-NMR: δ = 1.18–2.80 (m; 8H, $-(CH_2)_4-$), 3.76, 3.78 (2s; each 3H, $2CO_2Me$), 5.76 (dm, *J* = 6.5 Hz; 1H, 12-H), 6.27 (d, *J* = 6.2 Hz; 1H, 9-H), 6.34 (dd, *J* = 11.2, 6.2 Hz; 1H, 10-H), 6.45 (dd, *J* = 11.2, 6.5 Hz; 1H, 11-H), 6.66 (br. s; 1H, 1-H), 7.45 (br. s; 1H, 4-H); UV: λ_{max} (lgε) = 253 sh (4.23), 266 (4.29), 341 (3.79) nm

6b: ^{1}H-NMR: δ = 1.18–2.70 (m; 8H, $-(CH_2)_4-$), 1.80 (d, *J* = 1.0 Hz; 3H, 10-Me), 1.98 (s; 3H, 12-Me), 3.75, 3.77 (2s; each 3H, $2CO_2Me$), 6.03 (s; 1H, 11-H), 6.12 (s; 1H, 9-H), 6.68 (s; 1H, 1-H), 7.41 (s; 1H, 4-H); UV: λ_{max} (lgε) = 225 sh (4.27), 239 sh (4.42), 275 (4.30), 340 (3.80), 404 sh (3.01) nm

7aA: ^{1}H-NMR: δ = 3.57, 3.64 (2s; each 3H, $2CO_2Me$), 5.73 (dd, *J* = 6.3, 1.1 Hz; 1H, 4-H), 6.10–6.35 (m; 5H, 5,6,7,9,10-H), 6.42 (ddd, *J* = 11.5, 5.5, 1.0 Hz; 1H, 11-H), 6.56 (d, *J* = 10.5 Hz; 1H, 8-H), 6.59 (d, *J* = 11.5 Hz; 1H, 12-H), 7.49 (d, *J* = 6.3 Hz; 1H, 3-H); UV: λ_{max} (lgε) = 233 (4.44), 257 sh (4.25), 308 (4.09), 372 sh (3.35) nm

7bA: ^{1}H-NMR: δ = 1.91 (d, *J* = 1.1 Hz; 3H, Me), 1.93 (d, *J* = 0.9 Hz; 3H, Me), 3.59, 3.64 (2s; each 3H, $2CO_2Me$), 5.73 (dd, *J* = 6.6, 1.1 Hz; 1H, 4-H), 5.95 (br. s; 1H, 11-H), 6.10–6.20 (m; 2H, 6,7-H), 6.21 (br. s; 1H, 9-H), 6.31 (dm, *J* = 10.7 Hz; 1H, 8-H), 6.55 (dd, *J* = 10.6, 1.2 Hz; 1H, 5-H), 7.51 (d, *J* = 6.6 Hz; 1H, 3-H); UV: λ_{max} (lgε) = 222 (4.43), 233 (4.44), 260 sh (4.26), 318 (3.94) nm

8bA: ^{1}H-NMR: δ = 1.85 (d, *J* = 0.9 Hz; 3H, 12-Me), 2.09 (d, *J* = 1.1 Hz; 3H, 10-Me), 3.98–4.01 (m; 2H, 1-CH_2O), 4.10 (dd, *J* = 13.3, 2.4 Hz; 1H, 2-CH_2O), 4.33 (ddd, *J* = 13.3, 5.2, 0.7 Hz; 1H, 2-CH_2O), 4.65 (t, *J* = 4.5 Hz; 1H, 1-OH), 4.93 (dd, *J* = 6.2, 5.2 Hz; 1H, 2-OH), 5.46 (d, *J* = 6.6 Hz; 1H, 4-H), 5.89, 5.99 (2br. s; each 1H, 9,11-H), 5.94–6.07 (m; 3H, 6,7,8-H), 6.35 (d, *J* = 11.4 Hz, 1H, 5-H), 6.46 (d, *J* = 6.6 Hz, 1H, 3-H); UV: λ_{max} (lgε) = 240 (4.48), 258 sh (4.29), 287 sh (3.94), 318 sh (3.67), 363 sh (3.34) nm

8bB: ^{1}H-NMR: δ = 1.57 (s; 3H, 12-Me), 1.90 (d, *J* = 1.1 Hz; 3H, 10-Me), 3.92 (dd, *J* = 12.9, 6.0 Hz; 1H, CH_2O), 3.98–4.19 (m; 2H, CH_2O), 4.30–4.38 (m; 1H, CH_2O), 4.71 (dd, *J* = 5.9, 5.0 Hz; 1H, OH), 4.81 (t, *J* = 5.6 Hz; 1H, OH), 5.30 (br. s; 1H, 9-H), 5.87 (d, *J* = 11.1 Hz; 1H, 8-H), 5.94–6.07 (m; 3H, 6,7,11-H), 6.23 (d, *J* = 11.8 Hz; 1H, 3-H), 6.35 (dd, *J* = 8.4, 3.0 Hz; 1H, 5-H), 6.36 (d, *J* = 11.8 Hz, 1H, 4-H)

X-ray analysis of **7a** and low temperature ^{1}H-NMR spectra of solutions of **7a** and **7b**, prepared at low temperatures, indicate that, as in **5** and **6**, only the π-bond-shift isomers with a single bond between the ester-substituted positions exist in solution and in the crystalline state. On the other hand, at room temperature there are signals of other isomers in the ^{1}H-NMR spectra with ratios of 9 : 2 : 1 in **7a** and 12 : 1 in **7b**. The complexity of the spectra as well as the unfavorable isomer distribution have so far thwarted any unequivocal structural assignments of the additional isomers formed at room temperature.

Reduction of the diester **7b** with diisobutylaluminum hydride (DIBAH) (THF, 0°C) affords the pure π-bond-

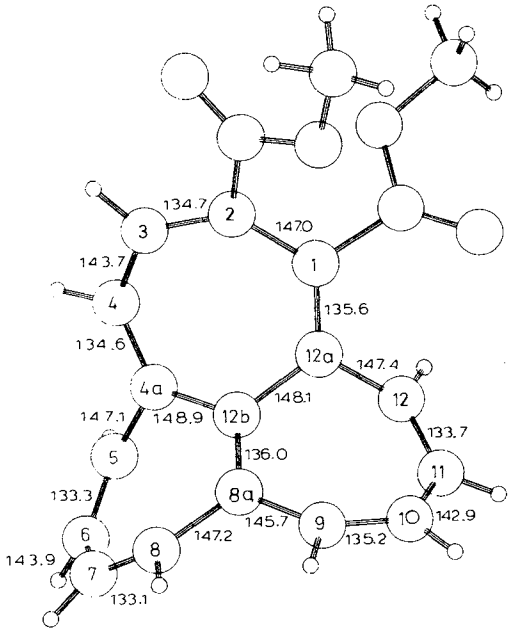
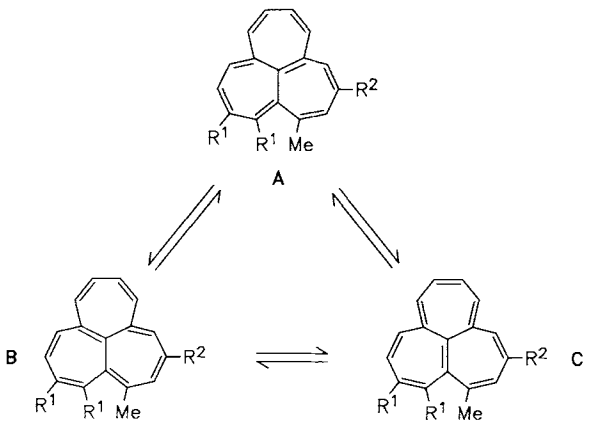


Fig. 1. Structure of **7a** in the crystal; bond lengths in pm (standard deviations: $\sigma_l = 0.4$ pm) [8].

shift isomer **A** of the diol **8b** (orange crystals, m.p. 178–179°C); in solution at room temperature an equilibrium is slowly established with the π-bond-shift isomer **B** (Table 1). Even at 150°C only the valence isomers **8bA** and **8bB** (1:1) are detectable in the ^{1}H-NMR spectrum. The free activation enthalpy for the isomerization **8bA** → **8bB** was found to be 24.1 kcal·mol^{-1} in [D$_6$]DMSO at 33°C.



8b: R^1 = CH_2OH, R^2 = Me; **9**: R^1 = Me, R^2 = H

These experimental results are consistent with π-SCF force field calculations[10] for the dynamics of the 1,2,12-trimethylcyclohepta[*ef*]heptalene **9**. Accordingly, the π-bond-shift isomer **9C**, in which the central double bond causes a partial planarization of the substituent-bearing carbon atoms, has an enthalpy of formation ca. 5 kcal·mol^{-1} higher than the other two isomers. Whereas the direct conversion of **9A** into **9B** should require an activation enthalpy of 38 kcal·mol^{-1}, the value for the isomerization of **9A** to **9C** is only 28 kcal·mol^{-1} and for the isomerization of **9C** to **9B** only 18 kcal·mol^{-1}. Hence, the observed conversion of **8bA** into **8bB** seems to proceed via the thermodynamically unstable isomer **8bC**. On the other hand, for a planarization of the tricycle **9**, i.e. for the transition state of the ring inversion, activation energies of ca. 70 kcal·mol^{-1} have been calculated. Consequently, a ring inversion in case of **7b** and **8b** may require temperatures at which these compounds are presumably no longer stable.

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3a, 51381-34-1; **3b**, 51381-54-5; **4a**, 7140-38-7; **4b**, 101998-79-2; **5a**, 101998-80-5; **5b**, 101998-81-6; **6a**, 101998-82-7; **6b**, 101998-83-8; **7a**, 101998-84-9; **7b**, 101998-85-0; **8b**, 102046-58-2; $Cl(CH_2)_2CONMe_2$, 17268-49-4; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5.

[1] a) H. Irngartinger, M. Nixdorf, *Angew. Chem. 95* (1983) 415; *Angew. Chem. Int. Ed. Engl. 22* (1983) 403; G. Maier, H.-O. Kalinowski, K. Euler, *ibid. 94* (1982) 706 and *21* (1982) 693; b) J. F. M. Oth, *Pure Appl. Chem. 25* (1971) 573, and references cited therein; L. A. Paquette, *ibid. 54* (1982) 982, and references cited therein; c) K. Hafner, H. U. Süss, *Angew. Chem. 85* (1973) 626; *Angew. Chem. Int. Ed. Engl. 12* (1973) 575; B. Kitschke, H. J. Lindner, *Tetrahedron Lett. 1977*, 2511; P. Bischof, R. Gleiter, K. Hafner, K. H. Knauer, J. Spanget-Larsen, H. U. Süss, *Chem. Ber. 111* (1978) 932; d) E. Vogel, J. Wassen, H. Königshofen, K. Müllen, J. F. M. Oth, *Angew. Chem. 86* (1974) 777; *Angew. Chem. Int. Ed. Engl. 13* (1974) 732; L. A. Paquette, *Isr. J. Chem. 20* (1980) 233; K. Hafner, H. Diehl, H. U. Süss, *Angew. Chem. 88* (1976) 121; *Angew. Chem. Int. Ed. Engl. 15* (1976) 104.

[2] D. Lloyd: *Nonbenzenoid Conjugated Carbocyclic Compounds*, Elsevier, Amsterdam 1984, and references cited therein.

[3] Theoretical studies: A. Streitwieser, Jr.: *Molecular Orbital Theory for Organic Chemists*, Wiley, New York 1961, p. 290f; T. Nakajima: *Molecular Orbitals in Chemistry, Physics, and Biology*, Academic Press, New York 1964, p. 451; R. Zahradnik in J. P. Snyder (Ed.): *Nonbenzenoid Aromatics, Vol. 2*, Academic Press, New York 1971, p. 1; B. A. Hess, Jr., L. J. Schaad, *J. Org. Chem. 36* (1971) 3418; F. Tomas, J. I. Fernandez-Alonso, *An. Quim. 72* (1976) 122; I. Gutman, M. Milun, N. Trinajstić, *J. Am. Chem. Soc. 99* (1977) 1692; J. P. Gastmans, D. F. Gastmans, M. H. Mendes Ferraz, *Tetrahedron 33* (1977) 2205.

[4] Unsuccessful attempted syntheses: R. B. Woodward, T. Fukunaga, R. C. Kelly, *J. Am. Chem. Soc. 86* (1964) 3162; H. Butenschön, A. de Meijere, *Tetrahedron Lett. 25* (1984) 1693.

[5] K. Hafner, G. L. Knaup, H. J. Lindner, H.-C. Flöter, *Angew. Chem. 97* (1985) 209; *Angew. Chem. Int. Ed. Engl. 24* (1985) 212; W. Bernhard, P. Brügger, J. F. Daly, P. Schönholzer, R. H. Weber, H.-J. Hansen, *Helv. Chim. Acta 68* (1985) 415; W. Bernhard, P. Brügger, P. Schönholzer, R. H. Weber, H.-J. Hansen, *ibid. 68* (1985) 429.

[6] K. Hafner, H. Pelster, H. Patzelt, *Justus Liebigs Ann. Chem. 650* (1961) 80; K. Hafner, *Pure Appl. Chem. 28* (1971) 153; K. Hafner, K.-P. Meinhardt, W. Richarz, *Angew. Chem. 86* (1974) 235; *Angew. Chem. Int. Ed. Engl. 13* (1974) 204.

[7] All the compounds gave correct elemental analyses.

[8] G. L. Knaup, *Dissertation*, Technische Hochschule Darmstadt 1985.

[9] **7a**: Monoclinic, space group $P2_1/n$, $Z = 4$, $a = 1442.4(4)$, $b = 785.6(2)$, $c = 1462.4(4)$ pm, $\beta = 95.56(1)°$, $V = 1.649 \times 10^9$ pm^3, $\rho_{calc} = 1.290$ g/cm^3; $3° \le 2\theta \le 45°$; ($Mo_{K\alpha}$; $\lambda = 71.07$ pm); 2009 independent reflections, Lorentz and polarization corrections, position of the hydrogen atoms refined; disorder in the region of ester group at C1 (two positions for one oxygen with occupation numbers 0.9 and 0.1), $R_1 = 0.045$, $R_2 = 0.042$ for 1862 structure factors ($|F_o| \ge 2\sigma_F$). Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 on quoting the depository number CSD-51912, the names of the authors, and the full citation of the journal.

[10] H. J. Lindner, *Tetrahedron 30* (1974) 1127; Program PIMM 82, unpublished, Technische Hochschule Darmstadt 1982.

A Stable Monocyclic 1,4-Thiazepine: Synthesis and Characterization of 2,7-Di-*tert*-butyl-5-methoxy-1,4-thiazepine

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Currently, there is a great deal of interest in seven-membered heterocycles such as oxepins, azepines, and thie-

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