

pound also results from reaction of (1) with (4) in boiling tetralin (yield 17%), probably also *via* (7) as intermediate.

In contrast to (1), 4,6,8-trimethylazulene (11) reacts with (4) only in boiling tetralin; cycloaddition is hindered by the alkyl groups in positions 4 and 8.

The major product isolated was found to be 15% of the dihydrocyclopentaindene derivative (14) (yellow platelets,

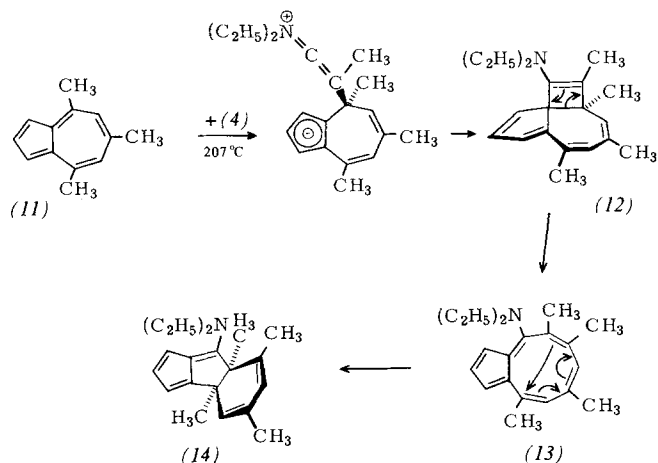


Table 1. Spectroscopic data of (7), (9), (10), and (14).

Cpd.	100 MHz- ¹ H-NMR (δ , J) in CDCl ₃	UV. λ_{max} [nm] (log ϵ) in <i>n</i> -hexane
(7) [a]	6.37 (dd, $J_1 = 4.5$ Hz, $J_2 = 2$ Hz; 1H), 6.2–5.6 (m, 5H), 4.9–4.7 (m, 1H), 3.2–2.8 (m, 1H), 2.97, 2.93 (q, $J = 7$ Hz; 4H, CH ₂ –CH ₃), 1.70 (d, $J = 2$ Hz; 3H, CH ₃), 0.98 (t, $J = 7$ Hz; 6H, CH ₂ –CH ₃)	328 (3.09) sh, 259 (3.89)
(9)	6.8–6.5 (m, 1H), 6.65, 6.25 (d, $J = 4.5$ Hz; 2H), 6.0–5.6 (m, 2H), 5.5–5.4 (m, 1H), 4.9–4.0 (m, 6H), 1.48 (d, $J = 7$ Hz; 3H, CH ₃), 1.30 (t, $J = 7$ Hz; 6H, CH ₂ –CH ₃)	400 (3.62), 336 (4.25), 319 (4.13) sh, 273 (4.08), 267 (4.04) sh, 252 (3.89) sh, 213 (4.16)
(10)	7.61 (d, $J = 10$ Hz; 1H), 7.2–6.4 (m, 3H), 3.7–3.2 (m, 4H, CH ₂ –CH ₂), 3.46 (q, $J = 7$ Hz; 4H, CH ₂ –CH ₃), 2.52 (s, 3H, CH ₃), 1.16 (t, $J = 7$ Hz; 6H, CH ₂ –CH ₃)	530 (2.51), 436 (4.06), 429 (3.89) sh, 410 (3.88), 403 (3.75) sh, 392 (3.59) sh, 363 (3.61) sh, 337 (3.83) sh, 316 (4.75), 306 (4.58) sh, 295 (4.26) sh, 256 (4.17), 224 (4.10) sh
(14)	6.55 (dd, $J_1 = 4$ Hz, $J_2 = 2.5$ Hz; 1H), 6.16 (dd, $J_1 = 4$ Hz, $J_2 = 1$ Hz; 1H), 5.80 (dd, $J_1 = 2.5$ Hz, $J_2 = 1$ Hz; 1H), 5.60, 5.44 (mc, 2H), 3.9–3.3 (m, 4H, CH ₂ –CH ₃), 1.93, 1.65 (d, $J = 1.5$ Hz; 6H, CH ₃), 1.34, 1.16 (s, 6H, CH ₃), 1.28 (t, $J = 7$ Hz; 6H, CH ₂ –CH ₃)	333 (4.24), 266 (3.84), 217 (3.98) sh

[a] 25.2 MHz-¹³C-NMR (δ) in CDCl₃: 165.8 (quart. C), 140.7 (2 quart. C), 135.3, 135.1, 130.5, 124.3 (1 C–H each), 122.8 (2 C–H), 115.6 (C–H), 69.1 (quart. C), 47.4 (2 CH₂–CH₃), 44.2 (C–H), 13.8 (2 CH₂–CH₃), 13.2 (CH₃).

m. p. 123–124°C; see Table 1)^[8], containing a resonance-stabilized aminofulvene moiety whose structure was established by spectroscopy and X-ray studies^[9]. This thermally induced reaction should also involve initial formation of the primary adduct (12) analogous to (5), which for steric reasons related to its substituents is no longer capable of 1,5 sigmatropic ring expansion but instead undergoes valence isomerization to the likewise unstable cyclopentacyclononene system (13). Valence isomerization in a manner characteristic of cyclononatetraene derivatives^[10] ultimately gives the thermally stable systems (14).

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(1), 275-51-4; (4), 4231-35-0; (5), 69258-21-5; (6), 69278-32-6; (7), 69258-22-6; (8), 69258-23-7; (9), 69258-24-8; (10), 69278-31-5; (11), 941-81-1; (12), 69258-25-9; (14), 69258-26-0

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- [2] a) W. Treibs, Naturwissenschaften 52, 452 (1965); b) R. Huisgen, Acc. Chem. Res. 10, 117 (1977), and references cited therein; c) K. Hafner, H. Diehl, H. U. Süss, Angew. Chem. 88, 121 (1976); Angew. Chem. Int. Ed. Engl. 15, 104 (1976).
- [3] We have observed a corresponding reaction sequence on treatment of the aceheptylene system with the ynamine (4): K. Hafner, H. Diehl, W. Richarz, Angew. Chem. 88, 125 (1976); Angew. Chem. Int. Ed. Engl. 15, 108 (1976); K. Hafner, H. D. Diesel, W. Richarz, *ibid.* 90, 812 (1978) and 17, 763 (1978).
- [4] All new compounds gave correct elemental analyses and mass spectra.
- [5] Triclinic needles P $\bar{1}$. $a = 1773(1)$, $b = 1231(1)$, $c = 680.7(5)$ pm, $\alpha = 101.00(5)$, $\beta = 85.94(5)$, $\gamma = 106.63(5)^\circ$, $Z = 2$; 2148 observed reflections with $|F| > 2\sigma_F$ (STOE two circle diffractometer, CuK α radiation $\lambda = 154.18$ pm); refined to $R = 0.108$ [11].
- [6] Dimerization of 1,3-di-*tert*-butylpentalene-5-carbaldehyde, -5-carbonitrile, and -5-carboxylic methyl ester, as well as cycloreversion of the dimers have similarly low activation energies (M. Suda, K. Hafner, Tetrahedron Lett. 1977, 2449).
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- [8] In addition, 9% of an isomer (colorless leaflets, m. p. 86°C) of (14) is isolated, which is probably a diethylamino(tetramethyl)dihydro-s-indacene.
- [9] Orthorhombic platelets, P2₁2₁2₁, $a = 1675(1)$, $b = 1331(1)$, $c = 754.6(5)$ pm, $Z = 4$; 764 observed reflections with $|F| > 2\sigma_F$ (STOE two circle diffractometer, CuK α radiation $\lambda = 154.18$ pm); refined to $R = 0.070$ [11].
- [10] G. Boche, H. Böhme, D. Martens, Angew. Chem. 81, 565 (1969); Angew. Chem. Int. Ed. Engl. 8, 594 (1969); G. Boche, H. Weber, D. Martens, A. Bieberbach, Chem. Ber. 111, 2480 (1978), and references cited therein.
- [11] G. M. Sheldrick, SHELX-76, unpublished.

Facile Ring Enlargement of Azulene to Give the Cyclopentacyclononene System by Dipolar Cycloaddition^[**]

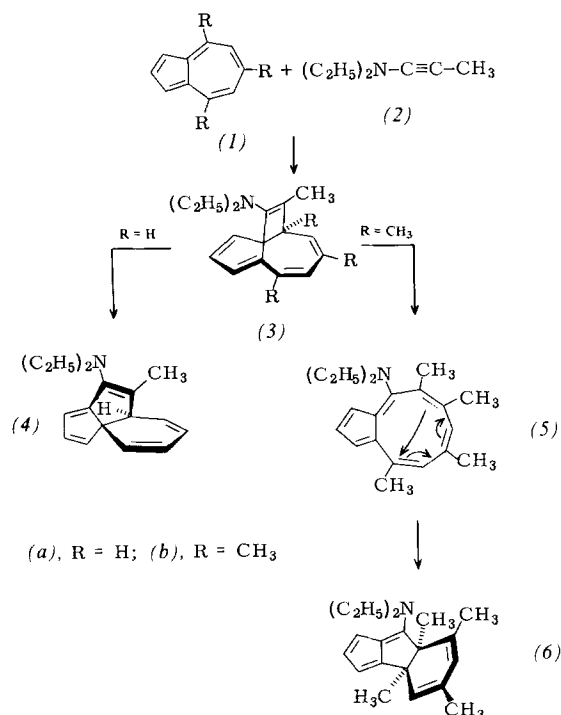
By Klaus Hafner, Hans Jörg Lindner, and Werner Ude^[*]

Azulene (1a) and 4,6,8-trimethylazulene (1b) react with 1-(diethylamino)propyne (2) to form 1,3-diene-bridged spiro-[3.4]octa-1,5,7-triene derivatives (3), which undergo stabilization by 1,5 sigmatropic ring enlargement to bridged spiro-[4.5]decatetraene (4) or by valence isomerization *via* the cyclopentacyclononene (5) to give the dihydrocyclopentaindene derivative (6)^[1a]. Owing to the valence isomerization characteristic of cyclononatetraenes^[1b], the azulene-homologous cyclopentacyclononene system could not yet be isolated. This result prompted a study of cycloadditions of (2) with azulenes bearing substituents which hinder or rule out valence isomerization of the nine-membered ring in (5). Inspection of models suggested that the readily accessible 1,2-dihydrocyclopent[cd]azulene (7)^[2] should be particularly suitable for this purpose.

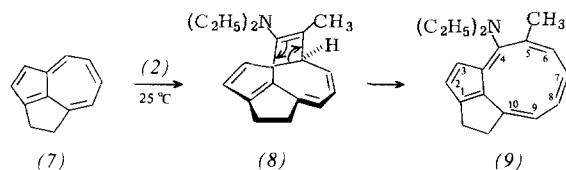
The bridged azulene (7) reacts like azulene with (2) at room temperature to give a brownish red crystalline 1:1

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adduct^[3] of m.p. 127–129°C [43% yield based on reacted (7)]. According to X-ray structure analysis (Fig. 1)^[4] and spectroscopic results, the expected 1,10-ethano-bridged 4-(diethylamino)-5-methylcyclopentacyclononene (9) is indeed formed.



The five-membered ring of the "6-amino-1-vinylfulvene system" present in (9) is planar, with an exocyclic double bond twisted through about 30° and a 1-vinyl group twisted only slightly out of the plane of the ring. The bond lengths in

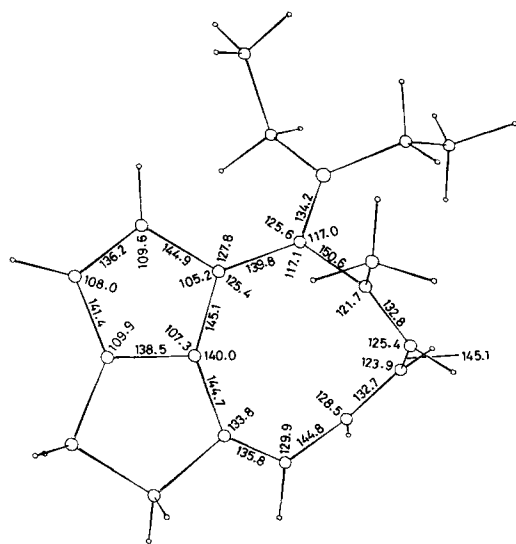


Fig. 1. Molecular structure of (9) with bond lengths [pm] and bond angles [°] of the cyclopentacyclononene system (standard deviations $\sigma_r = 0.4$ pm; $\sigma_\alpha = 0.4^\circ$).

this partial structure lie in the region characteristic of 6-amino-fulvenes^[5] and suggest extensive π -electron delocalization. The resulting weakening of the exocyclic double bond of the fulvene system is manifested in the relatively large twisting of this bond. The torsional angles of the other single bonds in the nine-membered ring (53, 83, 93°) are extremely large. The conformation of this ring resembles the tub form of cyclooctatetraene and thus corresponds to that of 1-(dimethylcarbamoyl)-azonine^[6].

UV/VIS and NMR spectra of (9) are in accord with this structure^[7]. The UV spectrum corresponds to that of 6-(dimethylamino)-1-(2-methoxyvinyl)fulvene^[8].

The novel ring system (9), presumably resulting by valence isomerization of the primary adduct (8), is the first cyclononacyclononene derivative which is thermally stable and inert towards atmospheric oxygen, and is not stabilized by benzo-annulation^[9]. No isomerization of (9) takes place in boiling toluene or in the presence of protic acids. Reversible protonation of (9), presumably occurring at one of the ring C atoms, is possible in 2 N H₂SO₄ and conc. acetic acid.

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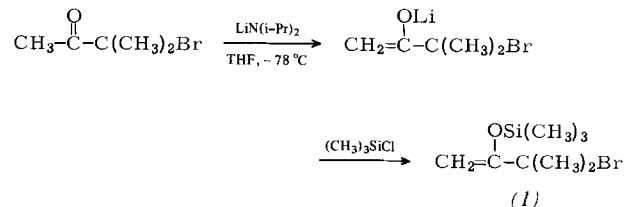
(2), 4231-35-0; (7), 14311-07-0; (9), 69258-16-8

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- [3] Elemental analysis and mass spectrum gave correct values.
- [4] Monoclinic prisms, P2₁/a, $a = 2088(1)$, $b = 866.7(5)$, $c = 899.1(5)$ pm, $\beta = 108.00(5)^\circ$, $Z = 4$. 1608 observed reflections with $|F| > 2\sigma_F$ (STOE two circle diffractometer, CuK α radiation $\lambda = 154.18$ pm); solution of structure and refinement with SHELX-76 (G. M. Sheldrick, unpublished), refined to $R = 0.069$.
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- [6] C. C. Chiang, I. C. Paul, A. G. Anastassiou, S. W. Eachus, J. Am. Chem. Soc. 96, 1636 (1974).
- [7] UV (*n*-hexane): $\lambda_{\text{max}} = 378$ (log $\epsilon = 4.09$), 320 (4.06), 293 sh (3.96) nm; 270 MHz-¹H-NMR (CDCl₃): $\delta = 6.49, 6.20$ (d, $J = 4.2$ Hz, H-2, H-3), 5.85, 5.25 (mc, 3H or 1H, H-6, 7, 8, 9), 3.8 (mc, 4H, CH₂-CH₃), 1.35 (t, 6H, $J = 7$ Hz, CH₂-CH₃), 1.75 (3H, CH₃), 3.15, 2.7 (mc, 1H or 3H, -CH₂-CH₂-); 25.2 MHz ¹³C-NMR (CDCl₃): $\delta = 166.5, 148.2, 145.2, 137.6, 135.3$ (1 quart. C each), 133.0 (1 C-H), 124.7 (2 C-H), 124.1, 121.3, 113.7 (1 C-H each), 108.3 (1 quart. C), 108.2 (1 C-H), 44.1 (2 CH₂-CH₃), 41.2, 25.9 (-CH₂-CH₂-), 23.3 (CH₃), 12.8 (2 CH₂-CH₃).
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3-Bromo-3-methyl-2-trimethylsiloxy-1-butene— A New Cycloaddition Reagent^[1]

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We have found that 3-bromo-3-methyl-2-trimethylsiloxy-1-butene (1) can be obtained in good yield from 3-bromo-3-



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