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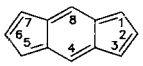
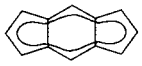
Synthesis and Properties of 1,3,5,7-Tetra-*tert*-butyl-*s*-indacene**

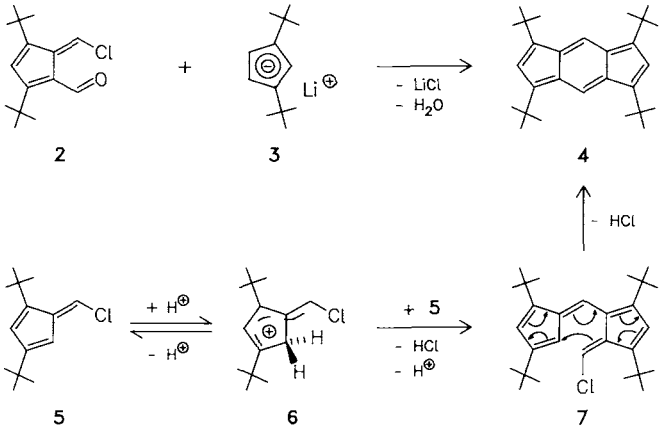
By *Klaus Hafner,* Bernd Stowasser, Hans-Peter Krimmer, Stefanie Fischer, Michael C. Böhm,* and *Hans Jörg Lindner*

According to quantum chemical calculations (MINDO/3 method) on *s*-indacene **1**[1]—a [12]annulene perturbed by two σ-bonds—substituents can be expected to have a strong influence on the bonding situation of the 12π perimeter. The enthalpy of formation for the localized structure **1A** with C_{2h}-symmetry and the corresponding structure of the 2,4,6,8-tetraalkyl derivatives is calculated ca. 10 kcal·mol^{-1} less than that for the delocalized structure **1B**

1A   1B

with D_{2h}-symmetry. For the 1,3,5,7-tetraalkyl-*s*-indacenes this energy gap should only be 2 kcal·mol^{-1}, whereas in the case of 4,8-diamino-*s*-indacenes a completely delocalized π-electron system should be preferred. Even nitrile groups in the 2- and 6-position can be expected to lower the energy difference between **1A** and **1B** to ca. 6 kcal·mol^{-1}. A similarly significant alkyl group effect, changing the bonding situation of the 12π perimeter of **1**, has so far never been reported in the case of other [4n]-π-electron systems. This effect is due to enhanced coupling between the π-electron system and the substituents in the case of the delocalized structure **1B**. The quantum chemical predictions could be experimentally established in the case of the stable 4,8-bis(dimethylamino)-*s*-indacene and the 4-dimethylamino-2,6,8-tri-*tert*-butyl derivative.[2,3] These results encouraged us to check the calculations also for pure alkyl derivatives of **1**, to gain more detailed information about the 12π-electron system. 1,3,5,7-Tetra-*tert*-butyl-*s*-indacene **4** seemed to be especially suitable for this purpose since it should be additionally stabilized kinetically by the bulky alkyl groups compared to the thermally extremely unstable **1**.[1]

In analogy to the synthesis of 4,8-bis(dimethylamino)-*s*-indacene, **4** can be obtained as red needles (decomp. 190°C; yield 30%)[3] by reaction of 2,4-di-*tert*-butyl-6-chloro-1-formylpentafulvene **2**[4] with lithium 1,3-di-*tert*-butylcyclopentadienide **3**[5] (CH_2Cl_2, 0°C). Recently we found an even more simple and rational entry to **4**, namely the protic acid-catalyzed condensation of 1,3-di-*tert*-butyl-6-chloropentafulvene **5**[6] in boiling methanol. The cation **6** formed on reversible protonation could be combined with **5** to give the 6-chloro-1-(6-pentafulvenyl)pentafulvene derivative **7**, whose 12π-electrocyclization with subsequent elimination of HCl led to **4** in 90% yield. Solid **4** is thermally stable as well as air-stable, but in solution it is extremely sensitive towards oxygen and traces of acid.[7]



The signals of the ring protons in the simple ^{1}H-NMR spectrum of **4** (see Table 1) are shifted to higher field in comparison to those of the dihydro derivative **9** ($\Delta\delta = 0.66$–0.81). This indicates a weak antiaromatic character of the *s*-indacene system. The ^{13}C-NMR spectrum, with four signals for the twelve perimeter C-atoms shows no temperature-dependence of the line shapes down to −130°C (in CS_2/COS (1 : 1)).[8] This suggests that either—in agreement with quantum chemical calculations—there is a low energy barrier between the two π-bond isomers, or the π-electron system is delocalized.

The crystal structure analysis of **4** at room temperature (see Fig. 1) gives CC-bond lengths for the perimeter that

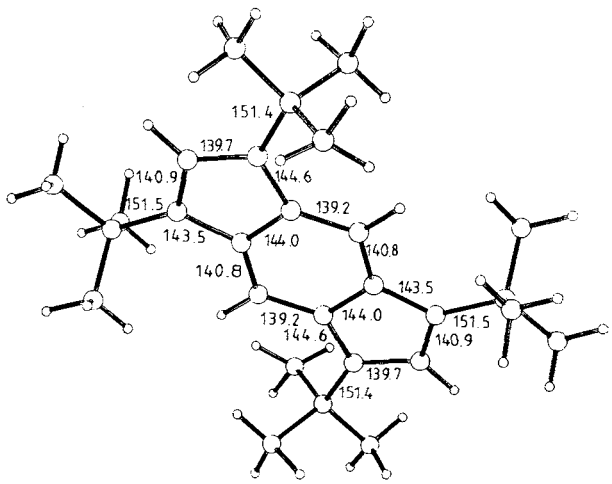


Fig. 1. Structure of **4** in the crystal at room temperature; bond lengths in pm (standard deviations $\sigma_r = 0.5$ pm). [10]

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are consistent with a delocalized state. However, as in the case of tetra-*tert*-butylcyclobutadiene,[9] an unequivocal proof of the structure can only be expected from a diffraction experiment at low temperatures.

An electronic spectrum calculated for the localized structure of **4** according to a modified INDO variant[11] (CI method) is in good agreement with the measured data (see Table 1).[12]

Table 1. Spectral data of the compounds **4**, **8**–**10**, and **13**–**15**. ^{1}H-NMR ($CDCl_3$, 300 MHz), ^{13}C-NMR ($CDCl_3$, 75.47 MHz), UV (*n*-hexane).

4: ^{1}H-NMR: $\delta = 1.18$ (s; 36 H, 4 *t*Bu), 5.29 (s; 2 H, 2,6-H), 6.90 (s; 2 H, 4,8-H); ^{13}C-NMR: $\delta = 31.2$ (q; *t*Bu), 34.0 (s; *t*Bu), 124.9 (d; C-2,6 or C-4,8), 129.1 (d; C-2,6 or C-4,8), 132.0 (s; C-3a,4a,7a,8a), 164.3 (s; C-1,3,5,7); UV: λ_{max} (lg ε) = 224 (4.10), 234 (4.03) sh, 278 (4.23) sh, 284 (4.37) sh, 289 (4.48) sh, 294 (4.61), 301 (4.66), 307 (4.77), 330 (3.45) sh, 340 (3.48), 451 (3.41) sh, 486 (3.83) sh, 500 (3.96) sh, 505 (4.01), 519 (4.11) sh, 527 (4.26) sh, 539 (4.51) sh, 545 nm (4.64)

8: ^{1}H-NMR: $\delta = 0.94$ (s; 9 H, *t*Bu), 1.00 (s; 9 H, *t*Bu), 1.26 (s; 3 H, Me), 1.36 (s; 9 H, *t*Bu), 1.38 (s; 9 H, *t*Bu), 3.09 (d, $J = 2.0$ Hz; 1 H, 7-H), 6.04 (s; 1 H, 2-H), 6.11 (d, $J = 2.0$ Hz; 1 H, 6-H), 7.53 (s; 1 H, 8-H), 7.66 (s; 1 H, 4-H); UV: λ_{max} (lg ε) = 230 (4.17) sh, 237 (4.43), 245 (4.65), 254 (4.64), 274 (3.64), 284 (3.63), 296 (3.60), 302 (3.53) sh, 308 (3.56), 313 (3.38) sh, 322 nm (3.27)

9: ^{1}H-NMR: $\delta = 0.67$ (d, $J = 6.7$ Hz; 3 H, Me), 1.22 (s; 9 H, *t*Bu), 1.29 (s; 9 H, *t*Bu), 1.30 (s; 9 H, *t*Bu), 1.32 (s; 9 H, *t*Bu), 3.40 (br. d, $J = 4.5$ Hz; 1 H, 3a-H), 3.89 (qd, $J_1 = 6.7$ Hz; $J_2 = 4.5$ Hz; 1 H, 4-H), 6.10 (s; 1 H, 6-H), 6.36 (d, $J = 1.2$ Hz; 1 H, 2-H), 7.56 (s; 1 H, 8-H); UV: λ_{max} (lg ε) = 235 (3.95), 241 (3.95), 286 (3.20) sh, 386 (4.30), 471 nm (2.76) sh

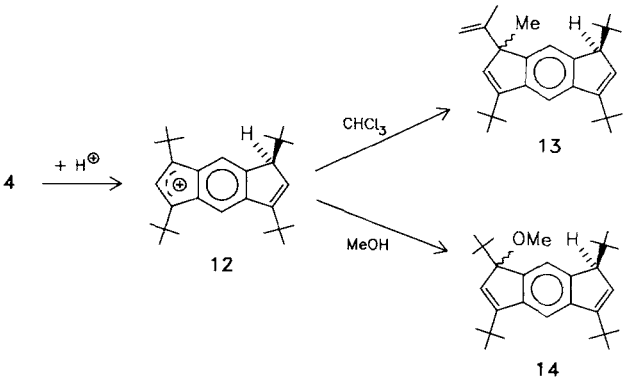
10: ^{1}H-NMR: $\delta = 1.01$ (s; 18 H, 2 *t*Bu), 1.40 (s; 18 H, 2 *t*Bu), 3.09 (d, $J = 1.9$ Hz; 2 H, 1,7-H), 6.13 (d, $J = 1.9$ Hz; 2 H, 2,6-H), 7.67 (s; 1 H, 4-H or 8-H), 7.73 (s; 1 H, 4-H or 8-H); UV: λ_{max} (lg ε) = 223 (4.06) sh, 230 (4.19) sh, 236 (4.43) 245 (4.61), 253 (4.55), 286 (3.82), 290 (3.82), 296 (3.84), 301 (3.78) sh, 307 (3.68) sh, 312 (3.53) sh, 321 nm (3.17)

13: ^{1}H-NMR: $\delta = 0.97$ (s; 9 H, *t*Bu), 1.38–1.40 (24 H, 2 *t*Bu, 2 Me), 3.10 (d, $J = 2.0$ Hz; 1 H, 7-H), 4.90 (m; 1 H, $=CH_2$), 5.10 (m; 1 H, $=CH_2$), 5.86 (s; 1 H, 2-H), 6.13 (d, $J = 2.0$ Hz; 1 H, 6-H), 7.32 (s; 1 H, 8-H), 7.70 (s; 1 H, 4-H); UV: λ_{max} (lg ε) = 229 (4.02) sh, 237 (4.26), 244 (4.49), 253 (4.50), 268 (3.50) sh, 278 (3.46) sh, 283 (3.43) sh, 296 (3.38), 301 (3.29) sh, 308 (3.40), 313 (3.14) sh, 321 nm (320)

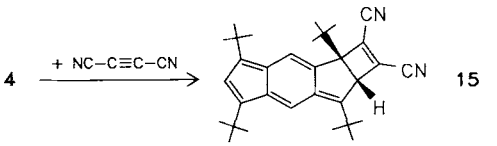
14: ^{1}H-NMR: $\delta = 0.99$ (s; 9 H, *t*Bu), 1.00 (s; 9 H, *t*Bu), 1.37 (s; 9 H, *t*Bu), 1.39 (s; 9 H, *t*Bu), 2.92 (s; 3 H, OMe), 3.09 (d, $J = 2.0$ Hz; 1 H, 7-H), 5.84 (s; 1 H, 2-H), 6.15 (d, $J = 2.0$ Hz; 1 H, 6-H), 7.48 (s; 1 H, 8-H), 7.60 (s; 1 H, 4-H); UV: λ_{max} (lg ε) = 227 (4.07) sh, 233 (4.23) sh, 240 (4.44), 248 (4.67), 257 (4.68), 281 (3.38), 288 (3.37) sh, 300 (3.27), 312 (3.20), 326 nm (3.03)

15: ^{1}H-NMR: $\delta = 1.12$ (s; 9 H, *t*Bu), 1.33 (s; 18 H, *t*Bu), 1.49 (s; 9 H, *t*Bu), 4.64 (s; 1 H, 2a-H), 6.41 (s; 1 H, 6-H), 7.31 (s; 1 H, 8-H), 7.74 (s; 1 H, 4-H); ^{13}C-NMR: $\delta = 26.0$–35.5 (*t*Bu), 60.5 ($C_{tert.}$), 67.4 ($C_{quart.}$), 111.2, 111.6 (C≡N), 121.4, 123.2 ($C_{tert.}$), 124.1, 129.5, 130.4 ($C_{quart.}$), 130.7 ($C_{tert.}$), 134.0, 137.8, 145.0, 145.4, 148.4, 155.3 ($C_{quart.}$); UV: $\lambda_{max} = 227$, 234 sh, 258 sh, 289, 308 sh, 358 sh, 369, 564, 582 sh, 650 nm sh

In its reaction with nucleophilic partners, **4** behaves—with exception of the formation of **9**—similarly to the 4,8-bis(dimethylamino)-*s*-indacene derivatives,[3] but contrary to these it is incapable of reversible protonation or Michael addition to electron-deficient alkynes. Whereas the addition of methyllithium (ether, 25 °C) leads to formation of 1,3,5,7-tetra-*tert*-butyl-1-methyl-1,7-dihydro-*s*-indacene **8** (colorless crystals, m.p. 200 °C; yield 46%) and its isomer **9** (brown crystals, m.p. 125 °C; yield 20%), the reduction with $LiAlH_4$ (tetrahydrofuran, 25 °C) gives 1,3,5,7-tetra-*tert*-butyl-1,7-dihydro-*s*-indacene **10** as major product along with 15% of the isomer **11** (both colorless crystals, subl. 218 °C). Protonation of **4** with methanesulfonic acid at room temperature affords the indenyl cation **12**,[13]



which rapidly undergoes a Wagner-Meerwein rearrangement in $CHCl_3$ to **13** (colorless crystals, m.p. 152 °C; yield 43%). In methanolic solution **12** can be trapped as the methyl ether **14** (colorless crystals, m.p. 195 °C; yield 62%). In boiling benzene, **4** combines with dicyanoacetylene to give



the [12+2]-cycloadduct **15** (blue powder, decomp. 40 °C; yield 9%), whose ring opening to the corresponding cyclohepta[*f*]indene has so far not been accomplished.

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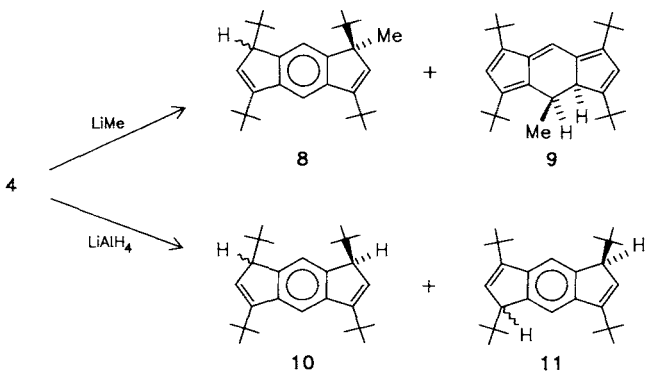
2, 101998-69-0; **3**, 101998-78-1; **4**, 101998-70-3; **5**, 85655-87-4; **8**, 101998-71-4; **9**, 101998-72-5; **10**, 101998-73-6; **11**, 101998-74-7; **13**, 101998-75-8; **14**, 101998-76-9; **15**, 101998-77-0; NCC≡CCN, 1071-98-3.



[1] K. Hafner, *Angew. Chem. 75* (1963) 1041; *Angew. Chem. Int. Ed. Engl. 3* (1964) 165; *Pure Appl. Chem. Suppl. 2* (1971) 1.
[2] K. Hafner, H.-P. Krimmer, *Angew. Chem. 92* (1980) 202; *Angew. Chem. Int. Ed. Engl. 19* (1980) 199.
[3] K. Hafner, *Pure Appl. Chem. 54* (1982) 939.
[4] H.-P. Krimmer, *Dissertation*, Technische Hochschule Darmstadt 1983.
[5] L. Knothe, H. Prinzbach, E. Hädicke, *Chem. Ber. 114* (1981) 1656.
[6] H.-P. Krimmer, B. Stowasser, K. Hafner, *Tetrahedron Lett. 23* (1982) 5135; K. Hafner, H.-P. Krimmer, B. Stowasser, *Angew. Chem. 95* (1983) 496; *Angew. Chem. Int. Ed. Engl. 22* (1983) 490.
[7] The data on the stability of **4** in [3] refer to solutions in organic solvents.
[8] We thank Prof. *K. Müllen*, Mainz, for recording the low-temperature ^{13}C-NMR spectra of **4**.
[9] H. Irngartinger, M. Nixdorf, *Angew. Chem. 95* (1983) 415; *Angew. Chem. Int. Ed. Engl. 22* (1983) 403.

[10] **4**: Monoclinic, space group $P2_1/c$, $Z=2$, $a=982.8(1)$, $b=1186.6(1)$, $c=1222.0(1)$ pm, $\beta=121.92(1)°$, $V=1.209\times10^9$ pm^3, $\rho_{calc}=1.142$ g/cm^3; $3°<2\theta<40°$ ($Mo_{K\alpha}$, $\lambda=71.07$ pm), 1052 independent reflections, Lorentz and polarization corrections, molecule at crystallographic inversion center, position of the hydrogen atoms calculated according to ideal geometry and optimized, anisotropic refinement of the carbon atoms, $R=0.070$, $R_w=0.048$ for 1048 structure factors ($|F|_0>0$). Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD-51911, the names of the authors, and the full citation of the journal.

[11] M. C. Böhm, R. Gleiter, *Theor. Chim. Acta 59* (1981) 127; calculated singlet-electron transitions of **4**: λ_{max}(oscillator strength) = 525 (0.15), 380 (0.02), 320 (0.36), 299 (0.75), 273 (0.07), 269 (0.27), 264 nm (0.30).

[12] T. Nakajima, T. Saijo, H. Yamaguchi, *Tetrahedron 20* (1964) 2119.

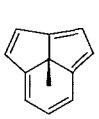
[13] Deuteration experiments show that **4** is protonated in the 2-position and the resulting cation then rapidly rearranges to **12**.

9b-Methyl-9b*H*-benzo[*cd*]azulene—A Novel Antiaromatic 12π-Electron System**

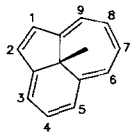
By *Klaus Hafner** and *Volker Kühn*

Dedicated to Professor Edgar Heilbronner on the occasion of his 65th birthday

Of the hitherto reported cyclic conjugated 12π-electron systems, only 1,7-methano-[12]annulene[1] allows conclusions to be drawn about the expected antiaromaticity of the planar 12π perimeter, since [12]annulene[2] and 1,6-methano-[12]annulene[3] are conformationally mobile and the π-perimeters deviate considerably from the planar geometry. In cycl[3.3.3]azine (9b-azaphenalene) and cycl[4.3.2]-azine[4] the properties of the perimeters are influenced by electronic interactions with the central nitrogen atom. Contrary to singly bridged annulenes multiple bridging of the perimeter should result in an increased planarity due to less transannular interactions and therefore allow a substantial delocalization of the peripheral π-electron system. In the case of the 10π-perimeter this expectation was confirmed by *Rees* et al.[5] with the synthesis of 7b-methyl-



1



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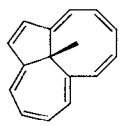

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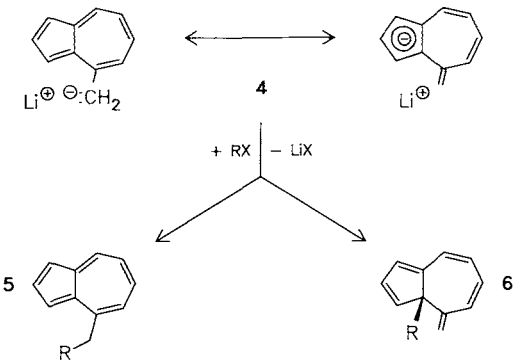
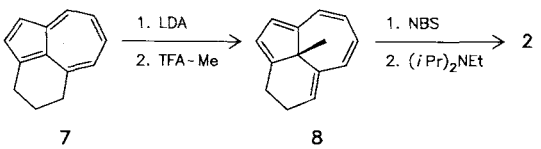
7b*H*-cyclopenta[*cd*]indene **1**. An unexpected reaction of 4-alkylideneazulenide salts **4** with electrophiles recently opened up a simple access to 9b-methyl-9b*H*-benzo[*cd*]-azulene **2**, the first tricyclic [12]annulene,[6] which proves to be an antiaromatic [12]annulene *par excellence* among the 12π-electron systems. At the same time, **2** fills the gap between the tricyclic annulenes **1** and **3**.[7]

Whereas reaction of the resonance-stabilized lithium 4-methyleneazulenide **4**[8] with primary alkyl halides in diethyl ether affords exclusively the 4-alkylazulenes **5**, reactions with *sec*- and *tert*-alkyl halides as well as with dimethyl sulfate or methyl trifluoromethanesulfonate (TFA-Me) lead chiefly to 3a-alkyl-3a,4-dihydro-4-methyleneazulenes **6** and small amounts of **5**, with removal of the azulenoid 10π-electron system.[9] The different regiochemical course of these reactions could be due to competing substitution mechanisms (S_N, SET).[10]



Also 4,5-dihydro-3*H*-benz[*cd*]azulene **7**,[11] after deprotonation with lithium diisopropylamide (LDA), reacts, like **4**, with dimethyl sulfate or TFA-Me to give the tricyclic pentaene **8** (yellow oil, yield 52%).[12] Bromination of **8**



with *N*-bromosuccinimide (NBS) in CCl_4 at 0°C yields an unstable bromo-derivative (yellow, oil), which is dehydrobrominated to **2** with diisopropylethylamine in tetrahydrofuran at room temperature without further purification. Thereby, the blue hydrocarbon **2** is obtained in ca. 30% yield; **2** is stable in solution up to 80°C. Solid **2** rapidly transforms into yellow high molecular products, even at −30°C.

Table 1. Spectral data of **2**, **8**, and **9**.

2A: 300-MHz ^{1}H-NMR ([D$_6$]DMSO): $\delta=3.88$ (d, $J=7.1$ Hz; 1H, 6-H), 3.98 (d, $J=5.8$ Hz; 1H, 3-H), 4.01 (d, $J=9.5$ Hz; 1H, 5-H), 4.18 (d, $J=6.7$ Hz; 1H, 9-H), 4.27–4.41 (m: $\delta=4.30$ (7-H), 4.37 (8-H), 4.39 (4-H)), 4.67, 4.69 (AB system, $J=5.8$ Hz; 2H, 1,2-H), 4.75 (s; 3H, Me); UV (*n*-hexane) (qualitative): $\lambda_{max}=262$, 286, 351, 368, 387 sh, 491 sh, 559 sh, 567 nm

8: 300-MHz ^{1}H-NMR ($CDCl_3$): $\delta=0.76$ (s; 3H, Me), 2.42–2.56 (m; 2H, 3-H), 2.81–2.93 (m; 2H, 4-H), 5.86–6.05 (m; 4H, 6-H or 9-H and 5,7,8-H), 6.18 (dd, $J=1.7$ Hz, $J=2.0$ Hz; 1H, 2-H), 6.43 (d, $J=1.7$ Hz; 1H, 1-H), 6.66 (d, $J=10.7$ Hz; 1H, 6-H or 9-H); UV (*n*-hexane): λ_{max}(lgε) = 262 (4.25), 266 (4.25), 289 sh (3.23), 304 sh (3.04), 350 sh (3.39), 370 sh (3.53), 384 (3.59), 402 sh (3.45) nm

9: 300-MHz ^{1}H-NMR ([D$_6$]DMSO): $\delta=1.07$ (s; 3H, Me), 5.87 (d, $J=10.4$ Hz; 1H, 9-H), 6.15 (dd, $J=6.5$ Hz, $J=10.4$ Hz; 1H, 8-H), 6.44 (dd, $J=6.5$ Hz, $J=11.5$ Hz; 1H, 7-H), 6.71 (d, $J=5.5$ Hz; 1H, 1-H), 6.79 (d, $J=5.5$ Hz; 1H, 2-H), 7.03 (d, $J=11.5$ Hz; 1H, 6-H), 7.20 (dd, $J=1.1$ Hz, $J=7.7$ Hz; 1H, 3-H or 5-H), 7.28 (dd, $J=7.1$ Hz, $J=7.7$ Hz; 1H, 4-H), 7.44 (dd, $J=1.1$ Hz, $J=7.1$ Hz; 1H, 3-H or 5-H); UV (*n*-hexane): λ_{max}(lgε) = 211 (4.12), 257 (4.34), 265 (4.38), 375 (3.61) nm

Proof of the structure of **2** is provided, in particular, by its ^{1}H-NMR spectrum[13] (see Table 1), which, at the same time, provides interesting insights into the bonding structure of this [12]annulene, which according to model considerations has a rigid planar structure. From the spec-

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