6,7-Dimethylene-2,4-diphenylbicyclo[3.2.1]oct-3-en-2-yl Anion. A Test for the Origin of the Unusual Properties of the Bicyclo[3.2.1]octa-3,6-dien-2-yl Anion

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On the basis of the ^{13}C NMR spectra of the 6,7-dimethylene-2,4-diphenylbicyclo[3.2.1]oct-3-en-2-yl anion **12**, which has been prepared in four steps from 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene **7**, and the 2,4-diphenylbicyclo[3.2.1]octa-3,6-dien-2-yl anion **11**, it seems reasonable to ascribe a bishomoaromatic character to **11**.

Due the work of Brown and Occolowitz[1] as well as Winstein *et al.*[2] the bicyclo[3.2.1]octadienyl anion **1** was regarded as the prototype of anionic homoaromaticity. Although its unusual properties are undisputed, quantumchemical calculations gave no evidence for a homoconjugation between the allyl anion and ethylene moiety.[3] In consequence, the pecularities of **1** have been attributed to an inductive effect, negative hyperconjugation and the interaction with the counter ion.[3c] By means of the NMR spectra of phenyl-substituted models, it has recently been shown that these effects cannot be of importance.[4] Being only slightly enhanced relative to that of the parent hydrocarbon **4**, the acidity of 3-phenylbicyclo[3.2.1]octa-2,6-diene **5** was taken as evidence against a homoaromatic stabilization in the corresponding anions **1** and **2**.[5] That this is not a necessary conclusion has been demonstrated previously on the occasion of the interpretation of the ^{13}C NMR spectrum of **2**.[6]

We report experimental evidence in favour of the homoaromatic nature of **1**, which is based on an orbital symmetry consideration. If **1** is homoaromatic, its special stabilization has to be ascribed to the interaction between the HOMO of the allyl anion and the LUMO of the ethylene moiety. In the 6,7-dimethylenebicyclo[3.2.1]oct-3-en-2-yl anion **3**, the interaction between the corresponding frontier orbitals is symmetry-forbidden. Thus, the acidity of the parent hydrocarbon **6** should be considerably reduced relative to that of **4**. However, experiments aimed at the determination of the pK_a value of **6** failed due to the sensitivity of the butadiene subunit toward strong nucleophiles.[7] Therefore, we have prepared and deprotonated the diphenyl derivative **10** of **6**. For the synthesis of **10**, the diphenylbicyclooctadiene **7**[8] served as starting material. It was transformed to the *cis*-glycol **8**,† which was converted into the α-diketone **9**‡ by a Swern oxidation. Finally, from **9**, triene **10**§ was obtained by applying the Nysted reaction.¶[9]

The acidity of **10** is dominated by the phenyl groups. By a competition experiment, the rates for the H/D exchange at C-4 of **10** and **7** were determined to have a ratio of 4 : 5.‖ Thus, triene **10** is somewhat less acidic than diene **7**. Trimitsis *et al.*[8,10] have shown that the corresponding rate ratio of diene **7** and 2,4-diphenylbicyclo[3.2.1]oct-2-ene **13** is 3 : 1. That the anion **11** of **7** clearly possesses characteristic properties of **1** is particularly manifest in the ^{13}C NMR spectrum (Scheme 1).[6,10] There, the signal of C-6,7 has experienced upfield shift, of 12.5 and 22.5 ppm relative to the C-6,7 absorptions of **7**. NMR data have proven to be valuable guides in the search for the best geometry of homoaromatic carbocations, which contain unusually shielded carbon atoms as well, by *ab initio* calculations of extremely high level.[11] The question was now whether the ^{13}C NMR spectrum of the anion **12** of **10**, with respect to the diphenylallyl part, is more similar to that of **11** or to that of the diphenylbicyclooctenyl anion **14**. The remarkable difference between **11** and **14** has been discussed previously.[4]

Triene **10** was deprotonated by using methyllithium in ether, and the NMR spectra of **12** were recorded in $[^2H_8]$THF.** The ^{13}C NMR spectrum (Scheme 1) reveals that C-2,4 and C-3 are shielded by 6.7 and 5.2 ppm, respectively, relative to these carbon atoms in **11** and deshielded by only 5.0 and 2.1 ppm, respectively, relative to these carbons in **14**. Also, the signals of the phenyl groups display a greater similarity between **12** and **14** than between **12** and **11**. Being smaller than those of **11**, the values of the *o*- and *p*-carbon atoms of **12** indicate somewhat more negative charge in the phenyl groups of **12**. These findings are at variance with the expectations based on inductive effects of and negative


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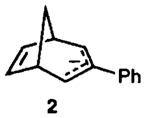

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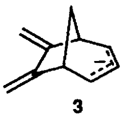
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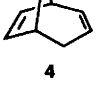
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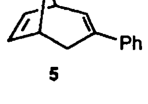

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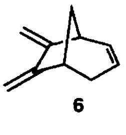
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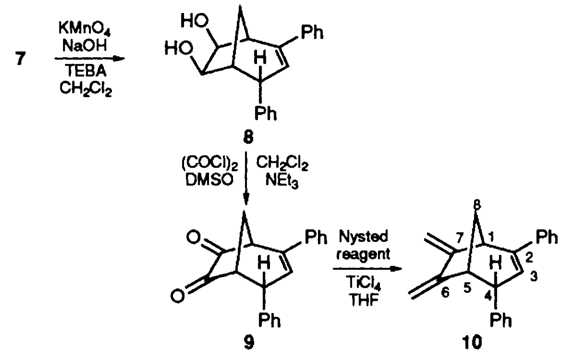

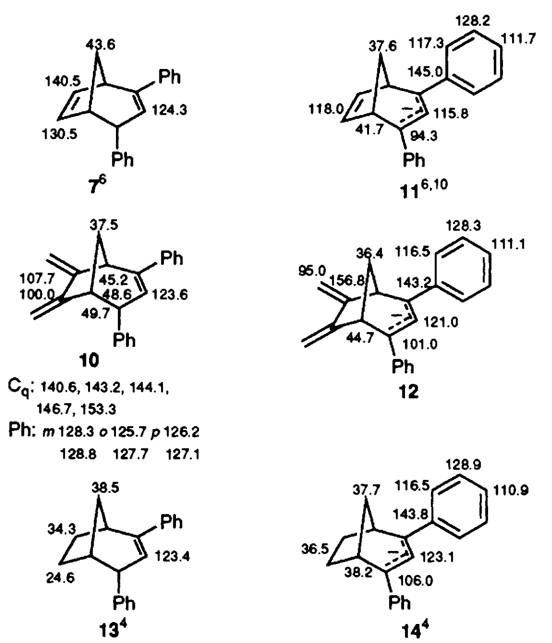

Scheme 1 ^{13}C NMR chemical shifts of the hydrocarbons **7**, **10**, and **13** ($CDCl_3$ as solvent) and the corresponding allyl anions (Li^+ as counter ion) **11**, **12** ($[^2H_8]$THF as solvent and internal reference, δ_{C-2} 67.4), and **14** ($[^2H_{10}]$DME as solvent and internal reference, δ_{C-1} 71.7)

hyperconjugation by C-6 and C-7 as origin of the unusual spectrum of **11**.

Highly interesting is the deprotonation effect on the ^{13}C chemical shifts of the butadiene subunit of **10**. In **12**, the quaternary carbon atoms (C-6,7) are deshielded by at least 3.5 and 10.1 ppm, whereas the methylene carbon atoms have experienced a shielding by 5.0 and 12.7 ppm. These shifts are rationalized by a polarization of the ethylene moieties under the influence of the negative charge, *i.e.* by a move of the electrons toward the methylene group to gain a larger distance from the allyl anion subunit.

Since the deprotonation effects on the butadiene carbon atoms of **10** sum up at best to a small net shielding, the much larger upfield shift of C-6,7 on conversion of **7** into **11** must have a different origin. Direct interactions C-2–C-7 and C-4–C-6 in the sense of a homoaromatic character of **11** offer the simplest explanation. Thereby, the coordination number of these carbon atoms is increased, thus changing their sp^2 hybridization somewhat toward sp^3.

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Footnotes

† 53% yield; mp 105–107 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.64 (br, 2 H, OH), 1.91 (br d, $J_{8,8}$ = 11.4 Hz, 8-H$_{syn}$), 2.41 (ddd, $J_{5,8anti}$ = 5.3, $J_{1,8anti}$ = 4.5 Hz, 8-H$_{anti}$), 2.46 (≈tt, $J_{4,5}$ = 4.3, $J_{1,5}$ = $J_{3,5}$ = 1.3 Hz, 5-H), 3.02 (dd, 1-H), 4.00 (dd, $J_{3,4}$ = 2.9 Hz, 4-H), 4.03, 4.22 (2 × dd, $J_{6,7}$ = 6.0, $J_{6,8syn}$ = $J_{7,8syn}$ = 1.2 Hz, 6-H, 7-H), 6.00 (dd, 3-H), 7.20–7.40 (m, 8 H), 7.50 (m, 2 H)(2 C$_6$H$_5$).

‡ 90% yield; mp 123–125 °C; IR (CCl$_4$) $\tilde{\nu}$/cm^{-1} = 1749, 1767 (C=O); UV (MeCN) λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) 474 (1.987), 310 (sh, 2.759), 248 (4.163), 216 (4.158); ^{1}H NMR (CDCl$_3$, 250 MHz) δ 2.49 (dt, $J_{8,8}$ = 12.3, $J_{1,8anti}$ = $J_{5,8anti}$ = 4.7 Hz, 8-H$_{anti}$), 2.62 (d, 8-H$_{syn}$), 3.13 (td, $J_{1,5}$ = 1.9 Hz, 5-H), 3.96 (dd, 1-H), 4.28 (dd, $J_{4,5}$ = 4.9, $J_{3,4}$ = 2.6 Hz, 4-H), 6.35 (d, 3-H), 7.06 (m, 2 H), 7.24–7.44 (m, 6 H), 7.56 (m, 2 H)(2 C$_6$H$_5$); this diketone was not stable in CDCl$_3$ solution and rearranged to an extent of 85% to 2,8*anti*-diphenylbicyclo[3.2.1]oct-2-en-6,7-dione within a month at room temperature.

§ 28% yield; colourless oil; MS (70 eV) *m*/*z* 284 (8%) [M$^+$], 220 (28), 206 (16), 205 (100), 189 (10), 177 (11), 168 (10), 167 (27), 165 (11), 91 (11), 81 (12), 57 (34), 41 (12); ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.16 (dt, $J_{8,8}$ = 10.7, $J_{1,8anti}$ = $J_{5,8anti}$ = 4.6 Hz, 8-H$_{anti}$), 2.21 (br d, 8-H$_{syn}$), 3.01 (br, t, 5-H), 3.59 (br d, 1-H), 4.13 (dd, $J_{4,5}$ = 4.5, $J_{3,4}$ = 2.8 Hz, 4-H), 3.97, 4.86, 5.15, 5.22 (4 × br s, 2 C=CH$_2$), 5.87 (br d, 3-H), 7.15 (m, 2 H), 7.18–7.42 (m, 6 H), 7.53 (m, 2 H) (2 C$_6$H$_5$); correct elemental analysis.

¶ The Nysted reagent[9] was purchased from Aldrich-Chemie GmbH & Co. KG. Its preparation from zinc and dibromomethane in THF is described in ref 9(*a*).

‖ A 1:1 mixture of **7** and **10** (0.11 mmol each) was dissolved in [^{2}H$_6$]DMSO (0.7 ml) and treated with two drops of a solution of sodium (10 mg) in CD$_3$OD (0.4 ml) at ambient temperature. ^{1}H NMR spectra taken after 2, 3, 8, 12, and 15 min indicated half-lives of 4 and 5 min for **7** and **10**, respectively.

** The procedure for the preparation of the NMR sample of **12** was that as described for **11** in ref.[6] ^{1}H NMR of **12** (200 MHz, the H-2 signal of [^{2}H$_7$]THF at δ 3.58 served as internal reference) δ 1.69–1.78 (m, 8-H$_2$), 3.38 (br s, 1,5-H), 4.67, 4.74 (2 × d, ^{2}J = 0.8 Hz, 2 C=CH$_2$), 5.89 (tt, ^{3}J = 6.8, ^{4}J = 1.5 Hz, *p*-H), 6.65 (m, *m*-H), 6.76 (m, *o*-H), 6.96 (s, 3-H).

References

1 J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 1965, 376; *J. Chem. Soc. B*; 1968, 411; J. M. Brown, *Chem. Commun.*, 1967, 638.

2 S. Winstein, M. Ogliaruso, M. Sakai and J. M. Nicholson, *J. Am. Chem. Soc.*, 1967, **89**, 3656.

3 (*a*) J. B. Grutzner and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1981, **103**, 1372; (*b*) E. Kaufmann, H. Mayr, J. Chandrasekhar and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, 1375; (*c*) P. v. R. Schleyer, E. Kaufmann, A. J. Kos, H. Mayr and J. Chandrasekhar, *J. Chem. Soc., Chem. Commun.*, 1986, 1583; (*d*) R. Lindh, B. O. Roos, G. Jonsäll and P. Ahlberg, *J. Am. Chem. Soc.*, 1986, **108**, 6554.

4 M. Christl and H. Müller, *Chem. Ber.*, 1993, **126**, 529.

5 G. Trimitsis, J. Rimoldi, M. Trimitsis, J. Balog, F.-T. Lin, A. Marcus, K. Somayajula, S. Jones, T. Hendrickson and S. Kincaid, *J. Chem. Soc., Chem. Commun.*, 1990, 237.

6 M. Christl and D. Brückner, *Chem. Ber.*, 1986, **119**, 2025.

7 W. N. Washburn, *J. Org. Chem.*, 1983, **48**, 4287.

8 G. B. Trimitsis and A. Tuncay, *J. Am. Chem. Soc.*, 1975, **97**, 7193.

9 (*a*) L. N. Nysted (G. D. Searle and Co.), *US Pat.* 3865848, 1975; *Chem. Abstr.*, 1975, **83**, 10406q; (*b*) *Aldrichimica Acta*, 1993, **26**, 14.

10 G. B. Trimitsis and P. Zimmerman, *J. Chem. Soc., Chem. Commun.*, 1984, 1506.

11 D. Cremer, F. Reichel and E. Kraka, *J. Am. Chem. Soc.*, 1991, **113**, 9459; D. Cremer, P. Svensson, E. Kraka, Z. Konkoli and P. Ahlberg, *J. Am. Chem. Soc.*, 1993, **115**, 7457.