Bull. Chem. Soc. Jpn., **56**, *2919—2921 (1983)*

Homoconjugation in Bicyclo[2.2.1]hept-2-en-7-yl and 1,4-Dihydro-1,4-methanonaphthalen-9-yl Radicals

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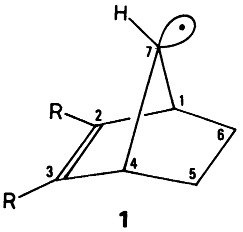
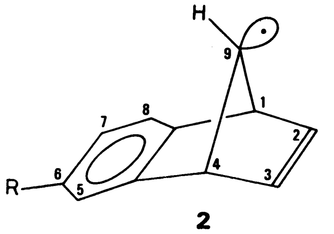
(Received March 28, 1983)

2,3-Dimethylbicyclo[2.2.1]hept-2-en-7-yl and 6-methyl-1,4-dihydro-1,4-methanonaphthalen-9-yl radicals are examined wiht ESR. Comparisons of their hyperfine splitting constants with those of bicyclo[2.2.1]hept-2-en-7-yl (**1a**) and 1,4-dihydro-1,4-methanonaphthalen-9-yl (**2a**) radicals show that the odd electron on the tervalent carbon atom is delocalized to the extent of 10% into the π system of the vinylene bridge in **1a**, and 5% at maximum into the π system of the phenylene bridge in **2a**, respectively. This odd eletron delocalization is accompanied by an increase of carbanion character of the tervalent carbon atom. The nonplanarity of their tervalent carbon atoms is discussed in relation to the carbanion character.

Molecules with bicyclo[2.2.1]hept-2-en-7-yl, 1,4-dihydro-1,4-methanonaphthalen-9-yl and related frameworks are of interest because of possible involvement of homoconjugation. In a previous communication,[1] the tervalent carbon atom of the bicyclo[2.2.1]hepta-2,5-dien-7-yl radical was shown to have a deep pyramidal geometry, which was proposed to arise mainly from intramolecular charge transfer interactions from the vinylene bridges onto the tervalent carbon atom. To estimate the extent of this type of charge transfer interaction, 2,3-dimethylbicyclo[2.2.1]hept-2-en-7-yl (**1b**) and 6-methyl-1,4-dihydro-1,4-methanonaphthalen-9-yl (**2b**) radicals are examined with ESR and compared with results of bicyclo[2.2.1]hept-2-en-7-yl (**1a**) and 1,4-dihydro-1,4-methanonaphthalen-9-yl (**2a**) radicals.



1
a : R = H
b : R = CH_3



2
a : R = H
b : R = CH_3

Results

The ESR spectrum of **1b** (Fig. 1) was observed during photolysis of a cyclopropane solution of a mixture of 7-bromo-2,3-dimethylbicyclo[2.2.1]hept-2-ene, triethylsilane, and di-*t*-butyl peroxide at −127 °C. The hyperfine structure of the spectrum arises from a proton (0.992 mT), two pairs of equivalent protons (0.173 and 0.161 mT), and six equivalent protons (0.140 mT). The *g* factor is 2.00240. On the basis of the comparison of these hyperfine splitting constants (hfsc) with those of **1a**,[2,3] the formers are assigned as shown below:

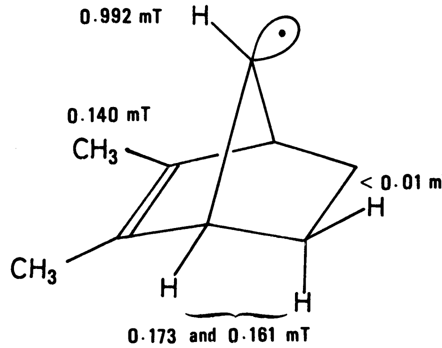


Figure 2 shows the ESR spectrum of **2b** generated similarly from 9-*anti*-bromo-6-methyl-1,4-dihydro-1,4-dihydro-1,4-methanonaphthalene. The spectrum consists of a doublet of 0.812 mT split into triplets of 0.166 mT further into quintets of 0.028 mT. By comparing these hfsc's with those of **2a**,[3] the formers can be most reasonably assigned as shown on the next page.

The hfsc's of phenylene protons and vinylene protons of **2a** could not be uniquely assigned in the previous communication[3] due to lack of sufficient data. The present assignment of phenylene proton hfsc of **2b** leads to following assignment of the observed hfsc's of **2a**:

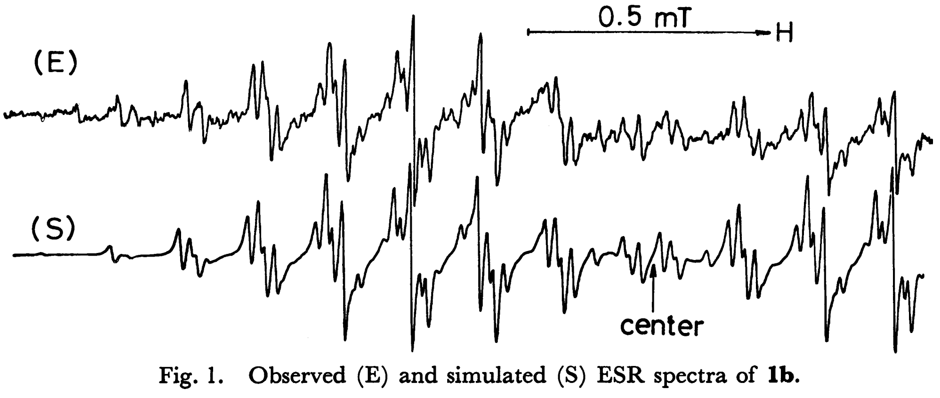


Fig. 1. Observed (E) and simulated (S) ESR spectra of **1b**.

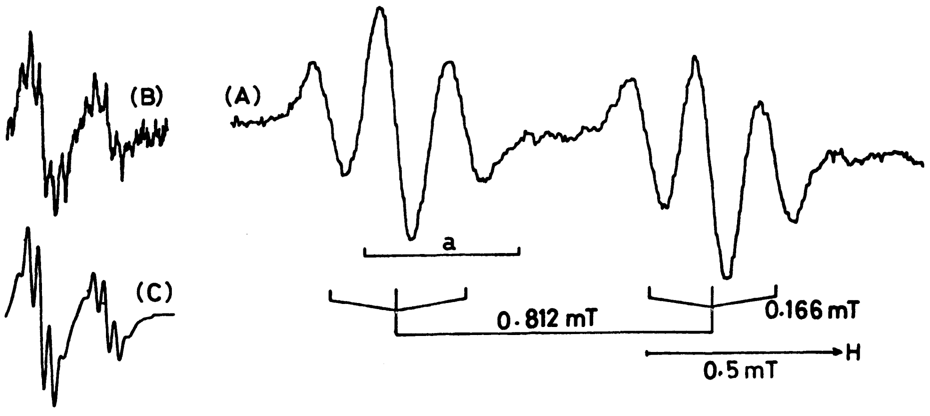
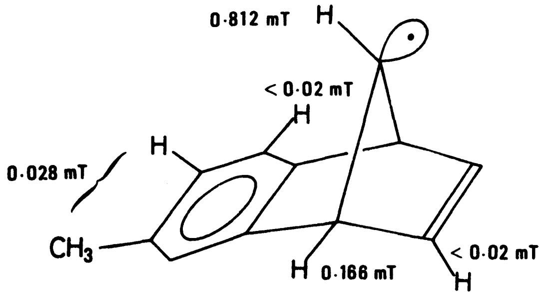
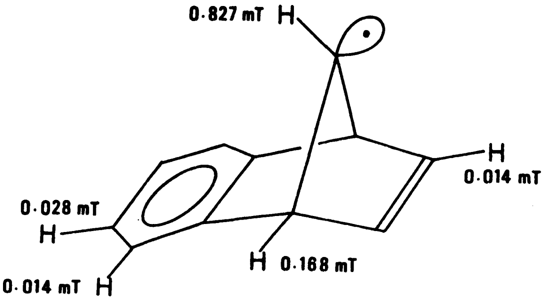


Fig. 2. (A) ESR spectrum of **2b**. (B) Underlined part a of (A) observed with higher resolution. (C) Simulated spectrum corresponding to (B).





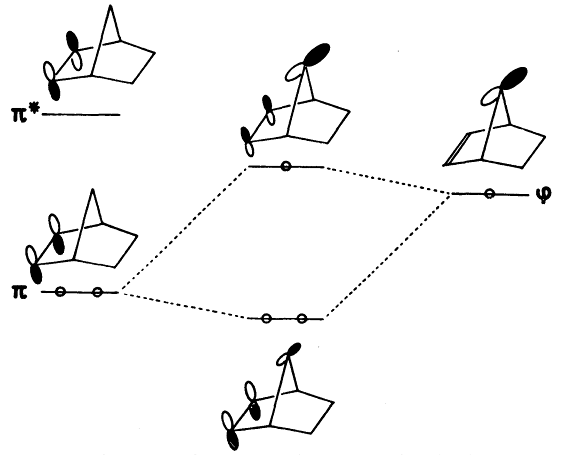


Fig. 3. Bishomocyclopropenyl conjugation in **1a** and **1b**. The mixing of π^* and φ is symmetry-forbidden.

Discussion

*Homoconjugation in **1a** and **1b**.* The bishomocyclopropenyl conjugation in **1a** and **1b** is the symmetry-allowed intramolecular charge transfer interaction from the vinylene π system to the tervalent carbon atom as shown in Fig. 3. This conjugation gives the tervalent carbon atom a carbanion character and delocalizes the odd electron onto a π atomic orbital of a vinylene carbon atom from the tervalent carbon atom. When the electron density of δ is transferred from the vinylene bridge onto the tervalent carbon atom, the odd electron density on a vinylene carbon atom is $\delta/2$ in the present simple model. If this mechanism is the major source of the hfsc of the vinylene proton of **1a** (0.12 mT),[2,3] this hfsc, $a(\mathrm{H}_2)$, can be correlated with the odd electron density, $\delta/2$, as

$$a(\mathrm{H}_2) = Q_\alpha\delta/2, \quad Q_\alpha = 2.3\ \mathrm{mT},$$

and the methyl proton hfsc of **1b**, $a(\mathrm{CH}_3)$, with $\delta/2$ as:

$$a(\mathrm{CH}_3) = Q_\beta\delta/2, \quad Q_\beta = 2.7\ \mathrm{mT}.$$

Both of the equations are satisfied when $\delta=0.10$, showing that both $a(\mathrm{H}_2)$ of **1a** and $a(\mathrm{CH}_3)$ of **1b** originate from the odd electron delocalization onto the vinylene π system from the tervalent carbon atom through the homoconjugation and that the extent of this delocalization is about 10%.

*Homoconjugation in **2a** and **2b**.* The bishomobenzocyclopropenyl conjugation in **2a** and **2b** is the symmetry-allowed mixing of the odd electron orbital on C_9 (φ) with phenylene orbitals of π_1, π_2, and π_3 shown in Fig. 4. Since the orbital energy difference between π_1 and φ is larger than those between φ and the other two π orbitals in Fig. 4, the mixing between π_1 and φ can be neglected for the present semiquantitative analysis of the homoconjugation.

Protons and/or those in the methyl moiety bonding to C_6 and C_7 of **2a** and **2b** have larger hfsc's than those of protons bonding to C_5 and C_8. This shows that the odd electron is delocalized onto π_2 rather than π_3. This mixing of the odd electron orbital on C_9, φ, with the doubly occupied π_2 orbital induces a carbanion character of the tervalent carbon atom. The extra electron density accumulated on the tervalent carbon atom by this bishomobenzocyclopropenyl conjugation is estimated from the phenylene proton hfsc's of **2a** and **2b** as 0.05 at maximum, which is smaller than that of the bishomocyclopropenyl conjugation in **1a** and **1b**.

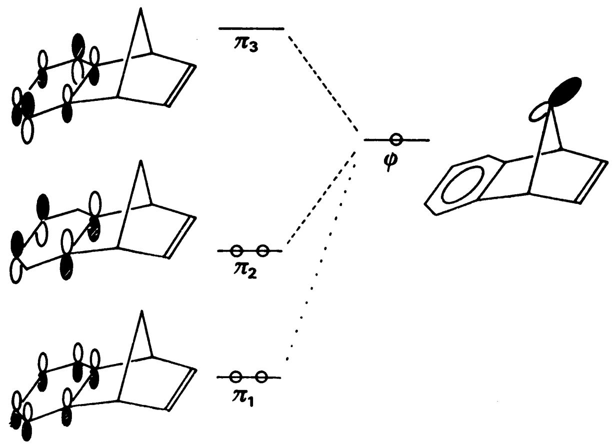


Fig. 4. Bishomobenzocyclopropenyl conjugation in **2a** and **2b**. The other three π molecular orbitals of the phenylene ring are symmetry-forbidden to interact with the odd electron orbital, φ.

The resolved small hyperfine splittings by H_5 and H_8 of **2a** indicate that there exists a minor mixing of π_3 into φ. This mode of interaction is stabilizing, but it transfers electron density from C_9 onto the phenylene π system. Therefore, even if the total electron density accumulated on the tervalent carbon atom by bishomobenzocyclopropenyl interaction is smaller than that by bishomocyclopropenyl interaction, the former can be more stabilizing than the latter.

Pyramidal Geometry of Tervalent Carbon Atom. The decrease of the α proton hfsc in the order of bicyclo[2.2.1]hept-7-yl radical (**3**) (1.678 mT),[2] 1,2,3,4-tetrahydro-1,4-methanonaphthalen-9-yl radical (**4**) (1.278 mT),[3] **1a** (1.087 mT),[2] **2a** (8.27 mT),[3] and bicyclo[2.2.1]hepta-2,5-dien-7-yl radical (**5**) (0.449 mT)[1] indicates the increase of the nonplanarity of the tervalent carbon atom, because these hfsc's have negative signs.[1,3] We suggested previously that the extent of the bending of the tervalent carbon atom of **3** and related radicals would correlate with the angle between C_1–C_7 and C_7–C_4 bonds.[3] However, the difference between C_1–C_7–C_4 angles of **3** and **5** is expected to be small, since the corresponding angle in bicyclo[2.2.1]heptane (93.2°) is only slightly larger than that of bicyclo[2.2.1]hepta-2,5-diene (92.0°).[4] It seems difficult to attribute the difference between the bendings of the tervalent carbon atoms of **3** and **4** entirely to the small difference between their C_1–C_7–C_4 bond angles.[1]

The introduction of methyl substituent(s) onto a bridging unsaturated moiety of **1a** or **2a** induces an increase of the nonplanarity of the tervalent carbon atom as shown by the decrease of their α proton hfsc's. Thus we propose that the increase of the nonplanarity of the tervalent carbon atom of **1a**, **1b**, **2a**, **2b**, **4**, and **5** from that of **3** would have been induced mainly by the increase of the carbanion character of their tervalent carbon atoms arising from homoconjugation(s). Indeed, the small bond angle of C_1–C_7–C_4 of **3** should be one of major factors inducing the pyramidal geometry of its tervalent carbon atom.

The geometry of the tervalent carbon atom of the radicals appearing in the present discussion suggests the following trends: (i) bishomocyclopropenyl interaction induces more carbanion character of the tervalent tarbon atom than bishomobenzocyclopropenyl interaction, but the latter is more stabilizing than the former; and (ii) a geometry in which the rear-lobe of the odd electron orbital on the tervalent carbon atom overlaps with the π orbital(s) of the bridging moiety is preferred than the geometry of the front-lobe overlap, but the extent of charge transfer by homoconjugation in the front-lobe overlap geometry is not negligibly small.

Experimental

The equipments and procedures for the photolysis-ESR experiments have been described earlier.[5]

7-anti-Bromo-2,3-dimethylbicyclo[2.2.1]hept-2-ene. 2,3-Dimethylbicyclo[2.2.1]hept-2-en-7-one (2.4 g, 0.18 mmol) was reduced to 7-hydroxybicyclo[2.2.1]hept-2-ene by $LiAlH_4$ in ether.[6] The alcohol, freed from ether, was dissolved into 20 ml of pentane without purification and shaken with 22 ml of 47% HBr aqueous solution for 10 min at room temperature. After evaporation of the pentane from the organic layer, *anti*-7-bromo-2,3-dimethylbicyclo[2.2.1]hept-2-ene (bp 95 °C/21 Torr)[7] was obtained in 42% yield based on the starting ketone. 60 MHz ^1H NMR (CCl_4): δ 1.10 (H_{5endo}, H_{6endo}). 1.63 (CH_3), 2.03 (H_{5exo}, H_{6exo}), 2.5 (H_1, H_4), 3.73 (H_{7syn}).

9-anti-Bromo-6-methyl-1,4-dihydro-1,4-methanonaphthalene. To a stirred solution of 6-methyl-1,4-dihydro-1,4-methanonaphthalene[8] (3.0 g, 19 mmol) in 11 ml of CCl_4 kept below 10 °C, bromine (3.4 g, 21 mmol) in 25 ml of CCl_4 was added dropwise in 10 min and stirred for 1 h at room temperature thenafter. After evaporation of the solvent and excess of the bromine, crude 2-*exo*,9-*anti*-dibromo-6-methyl-1,4-dihydro-1,4-methanonaphthalene was obtained as a viscous residue. The crude dibromide was reacted with potassium *t*-butoxide (2.2 g, 20 mmol) in dry dimethyl sulfoxide under nitrogen atmosphere at 70—80 °C for 1.5 h. The reaction mixture was poured into water and extracted with ether. After evaporation of the ether, the residue was recrystallized from ethanol to give 9-*anti*-bromo-6-methyl-1,4-dihydro-1,4-methanonaphthalene (1.1 g, 4.7 mmol) as white crystals. 220 MHz ^1H NMR (CCl_4) δ 2.25 (s, 3H), 3.95 (s, 2H), 4.28 (s, 1H), 6.58 (s, 2H), 6.67 (m, 1H), 6.95—7.00 (m, 2H). (s: singlet. m: multiplet.).

We are indebted to Drs H. Tanida and T. Tsushima (Shionogi Research Laboratory, Osaka) for the offer of 6-methyl-1,4-dihydro-1,4-methanonaphthalene.

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7) Torr = 133 Pa.

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