Hydrocarbon Anions with High Stability. Part 1. Syntheses and Properties of Extremely Stable Cyclopentadienide Ions with 7*H*-Dibenzo[*c*,*g*]fluorenylidenemethyl Substituents

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The title carbanions (**2a**$^-$ and **3a**$^-$) have been synthesized and found to be extremely stable as shown by E_{ox} −0.20 and −0.33 V and pK_a values of 3.3 and 4.7 for their conjugate acid hydrocarbons, respectively, and **2a**$^-$ is almost identically stable to the most stable all-hydrocarbon anion.

The highly stable all-hydrocarbon anions, **1a**$^-$,[1] **1b**$^-$,[2,3] **2b**$^-$,[4] **3b**$^-$ [2,3] (Fig. 1) and so on[5] have been synthesized, all containing dibenzofluorenylidenemethyl or fluorenylidenemethyl substituents which are able to contribute to the delocalization of the charge on the anion centre by cross-conjugation. Among them **1a**$^-$ is known to be the most stable hydrocarbon carbanion [pK_a (RH) 5.9 in aqueous HCl–DMSO [(dimethyl sulfoxide) (molar ratio 15:85)].[1] However, the central unit of **1a**$^-$ is a methyl anion [pK_a (RH) 56][6] which is much less stable than a cyclopentadienyl anion [pK_a (RH) 18.0][6] and indenyl anion [pK_a (RH) 20.1].[6] It could be anticipated that a hydrocarbon carbanion with the highest stability might be constructed by a combination of the most stable carbanion centre and most effective substituents for charge delocalization. In this work, cyclopentadienide and indenide ions **2a**$^-$ and **3a**$^-$ have been synthesized with dibenzofluorenylidenemethyl groups as the substitutions, and their stability evaluated from their oxidation potentials and pK_a values for their conjugate acids and compared with those for related carbanions.

The precursor hydrocarbon of **2a**$^-$, **2a**H, was synthesized by a stepwise reaction[†] of the bisimmonium salt **4**[7] with 7*H*-dibenzo[*c*,*g*]fluorenide **5**$^-$,[8] as a brown powder in 21.0% overall yield (Scheme 1), in a similar manner to the preparations described for compounds **1a**H,[1] **1b**H[2,3] and **2b**H.[4] An analogous reaction of 1-(dimethylamino)methylene-3-(dimethyliminiomethyl)indene perchlorate provided hydrocarbon **3a**H,[‡,9] a yellowish orange powder, in 32.8% overall yield (Table 1).

Although the structures of **2a**H and **3a**H can exist as six and three kinds of isomer, respectively (Figs. 2 and 3), ^{1}H and ^{13}C NMR spectroscopy (Table 1) indicate that the hydrocarbons have the structure shown as **C** (Fig. 2) for **2a**H and **A** or/and **B** (Fig. 3) for **3a**H.[§] The isomer **A** should be preferred to **B** for **3a**H in terms of the steric crowding.

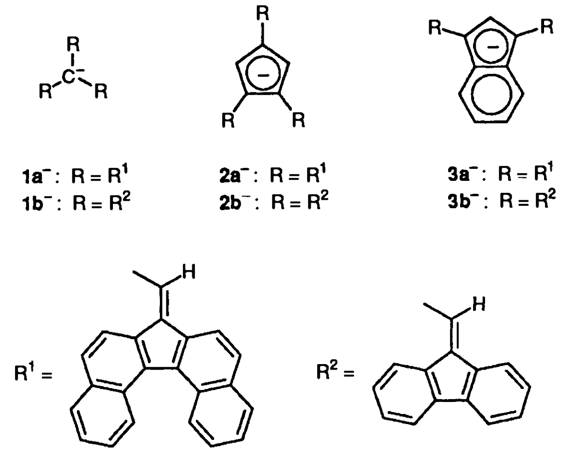

Fig. 1 All-hydrocarbon anions with high stability

Compound **2a**H dissociates completely into **2a**$^-$ in DMSO without any added base to show deep blue colour in analogy with **1a**H. Compounds **3a**H and **2b**H also dissociate spontaneously into **3a**$^-$ and **2b**$^-$ in DMSO, but their dissociation is not complete (K = 4.60 × 10^{-5} and 1.40 × 10^{-5} for **3a**H and **2b**H, respectively),[¶] whereas **3b**H does not dissociate under the similar conditions.

The maximum absorption bands for **2a**$^-$ and **3a**$^-$ are shifted to the much longer wavelength than those for **2b**$^-$ and **3b**$^-$ (Table 2), corresponding to the wider expansion of π-conjugation systems on both of the former.

The thermodynamic stability for **2a**$^-$ and **3a**$^-$ has been evaluated from the hydrocarbon acidity [pK_a (RH)] for their precursor hydrocarbons. The pK_a values for many carbon acids which are insoluble in water were usually estimated in DMSO solvents using the indicator method.[6,10] Those for **2a**H and **3a**H have been directly determined, in 90% aq. DMSO (v/v) containing various concentrations of HCl, by direct measurement of the pH values and the concentrations of the carbanions to indicate 3.3 and 4.7 (Table 2).[‖] For compounds **1a**H, **2b**H and **3b**H, the pK_a values have been shown to be 3.2 [5.9 in aq. HCl–DMSO (molar ratio 15:85)[1]], 6.3 and 7.6, respectively, by the same method. The accuracy of this method has been confirmed by the value for 9-cyanofluorene (Table 2).[**] These pK_a values demonstrate that (a) **2a**$^-$ is the most stable all-hydrocarbon cyclopentadienide ion and almost identically stable with **1a**$^-$ which was previously known as the most stable hydrocarbon anion[1] and (b) **3a**$^-$ is much more stable than **3b**$^-$ and **2b**$^-$ though it is not so stable

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[†] The disubstituted intermediate which was separated by MPLC (SiO$_2$) was not completely pure, but used in the next step without further purification: δ_H(60 MHz; CDCl$_3$) 3.15 (br s, 6 H) and 7.50–8.65 (m, 29 H); 56.3% yield.

[‡] The synthetic method for **3b**H (ref. 2) could not be applied for **3a**H.

[§] A methylene proton (δ 4.03) is observed as singlet and a signal (δ 49.0) for methylene carbon as a triplet on coupling mode for **2a**H and a methyne proton (δ 5.36) and carbon (δ 50.6), and an olefinic proton (δ 6.44) are all doublet for **3a**H.

[¶] Dissociation of 91% at 5.00 × 10^{-6} mol dm^3, 25 °C for **3a**H and 70% at 8.58 × 10^{-6} mol dm^{-3}, 25 °C for **2b**H.

[‖] Calculated by the use of the correlation pK_a = pH − log[R$^-$]/[RH]; the concentration of the carbanion has been measured by visible spectra.

[**] (i) The pK_a value (8.9) for 9-cyanofluorene by our method is in fair agreement with that (8.3) in DMSO by the indicator method (ref. 6); (ii) in the pK_a value between 9-cyanofluorene and **1a**H or **3b**H, almost equal differences (5.7 or 1.3) are observed by our method to those (5.5 or 1.4) observed by the previous method (ref. 3).

Table 1 Spectral and physical data for **2aH** and **3aH**

	2aH	**3aH**
Form	Dark brown powder	Yellowish orange powder
δ_H[a,b]	4.03 (s, 2 H), 7.23–8.05 and 8.22–8.65 (m, 40 H)	5.24 (d, 1 H, *J* 10.8), 6.44 (d, 1 H, *J* 10.8), 6.90–8.15 (m, 22 H)
δ_C[a,c]	49.0 (t), 118.1, 122.0, 122.4, 123.7, 124.8, 125.1, 125.5, 125.8, 126.6, 127.1, 127.3, 127.6, 128.3, 128.4, 128.7, 134.5, 134.8, 135.0, 136.1, 137.5, 138.0, 139.0, 139.7, 142.0, 145.3, 145.6, 147.6	50.6 (d), 118.2, 119.7, 120.3, 121.9, 122.7, 122.9, 125.0, 125.2, 125.4, 125.8, 126.0, 126.4, 126.9, 127.0, 127.2, 127.4, 127.7, 127.8, 128.5, 128.6, 128.8, 128.9, 130.7, 134.5, 134.9, 135.1, 135.4, 136.7, 136.8, 138.1, 138.3, 139.7, 139.9, 141.6, 142.0, 143.0, 145.0
ν/cm^{-1} [d]	3050w, 1580m, 1560m, 1510m, 1410m, 1400m, 1370m, 1340m, 1245m, 1220s, 1190s, 1150m, 1130m, 860m, 815vs, 750vs	3050m, 2980m, 1635m, 1515m, 1450m, 1350m, 1215m, 1135m, 1020w, 880s, 865s, 820vs, 760vs, 750vs, 700w
λ_{max}(CH_2Cl_2)/nm (log ε/dm^3 mol cm^{-1})	306 (7.2 × 10^4) 326sh (3.8 × 10^4) 427 (4.1 × 10^4) 526 (3.7 × 10^4)	228 (1.1 × 10^5) 353 (7.6 × 10^4) 314 (4.1 × 10^4) 333 (3.7 × 10^4) 349 (4.1 × 10^4) 364 (3.9 × 10^4) 412 (1.7 × 10^4)
M.p./°C (decomp.)	267.0–268.5	220.5–224.0
Found	C, 95.05; H, 4.6	C, 94.9; H, 4.6
(Calc.) (%)	(C, 95.27; H, 4.73)[e]	(C, 95.18; H, 4.82)[f]
Found M[g]	883	
Calc. *M*	895.12	

[a] In $CDCl_3$. [b] 270 MHz; *J*-values given in Hz. [c] 68 MHz; 28 and 38 signals were observed for **2aH** and **3aH** with 71 and 53 carbon atoms, respectively. [d] KBr disk. [e] For $C_{71}H_{42}$. [f] For $C_{53}H_{32}$. [g] By a vapour pressure equilibrium method.

Table 2 Oxidation potentials and λ_{max} for the carbanions and equilibrium acidity values (pK_a) and bond dissociation energies (E_d) for the conjugate acid hydrocarbons

Carbanion	pK_a[a,b]	E_{pa}[c]/V	E_d[b,d]/ kcal mol^{-1}	λ_{max}[e]/nm	log ε
1a$^-$	3.2 (5.9[f,g])	−0.18 (rev.)	73.5	697[g]	5.15[g]
1b$^-$	— (10.4[h])	—	—	647[i]	5.01[i]
2a$^-$	3.3 (—)	−0.20 (irrev.)	73.1	656	5.00
2b$^-$	6.3 (—)	−0.34 (irrev.)	74.0	590	4.84
3a$^-$	4.7 (—)	−0.33 (rev.)	72.0	784	4.96
3b$^-$	7.6 (10.0[h])	−0.53 (rev.)	71.4	694[j]	4.86[j]
9-Cyanofluorenide	8.9 (11.4,[h] 8.3[j])	—	—	—	—

[a] In 90% aq. DMSO (v/v) (see text); in parentheses: calculated using the indicator method. [b] For the corresponding conjugate acid. [c] Measured *vs.* Ag/Ag$^+$ in CH_3CN in the presence of tetrabutylammonium perchlorate as a supporting electrolyte; rev. reversible and irrev. irreversible. [d] E_d = 1.37pK_a + 23.1E_{ox} + 55.9 (refs. 6 and 11). [e] In DMSO, otherwise noted. [f] In aq. HCl–DMSO (molar ratio 15:85). [g] Ref. 1. [h] In DMSO–AcOH–AcONa; ref. 3. [i] In DMF; ref. 2. [j] In DMSO; ref. 6.

as **2a**$^-$ and **1a**$^-$. From these facts, it is concluded that (i) the replacement of fluorenylidenemethyl groups with dibenzofluorenylidenemethyl groups raises the stability of the carbanions by 3 pK_a units owing to the wider expansion of the π-conjugation systems and (ii) the stability of the carbanion is not enhanced by the replacement of the central methanide ion **1a**$^-$ with a cyclopentadienide ion, which could be ascribed to the inferior coplanarity of the whole π-conjugation system in **2a**$^-$ to that in **1a**$^-$.*

The oxidation potentials for **2a**$^-$ and **3a**$^-$ have been measured by a cyclic voltammetry (CV) method: $E_{pa} = -0.20$ and -0.33 V, respectively [*vs.* Ag/Ag$^+$ in CH_3CN with TBAP (tetrabutylammonium perchlorate) as a supporting electrolyte: Table 2]. For one-electron oxidation, **2a**$^-$ shows very similar stability to that of **1a**$^-$ (E_{ox} −0.18 V). A linear relationship, $E_{ox} = 18.2 - 1.18$pK_a ($r = 0.913$), can be found between the

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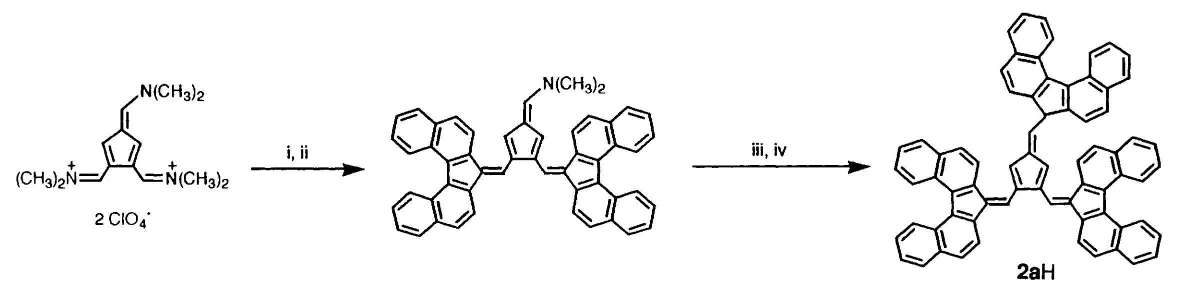
* Examined by the use of molecular models: Although all the three bulky substituent groups overlap with each other and are unable to be coplanar with the anion centre in **1a**$^-$ and **2a**$^-$, the angles of torsion of the substituents in the latter are larger than those in the former. On the other hand, the two substituents are coplanar in **3a**$^-$.



Scheme 1 *Reagents:* i, **5**H, NaOMe, pyridine; ii, H_2O; iii, **5**H, BuLi; iv, HCl

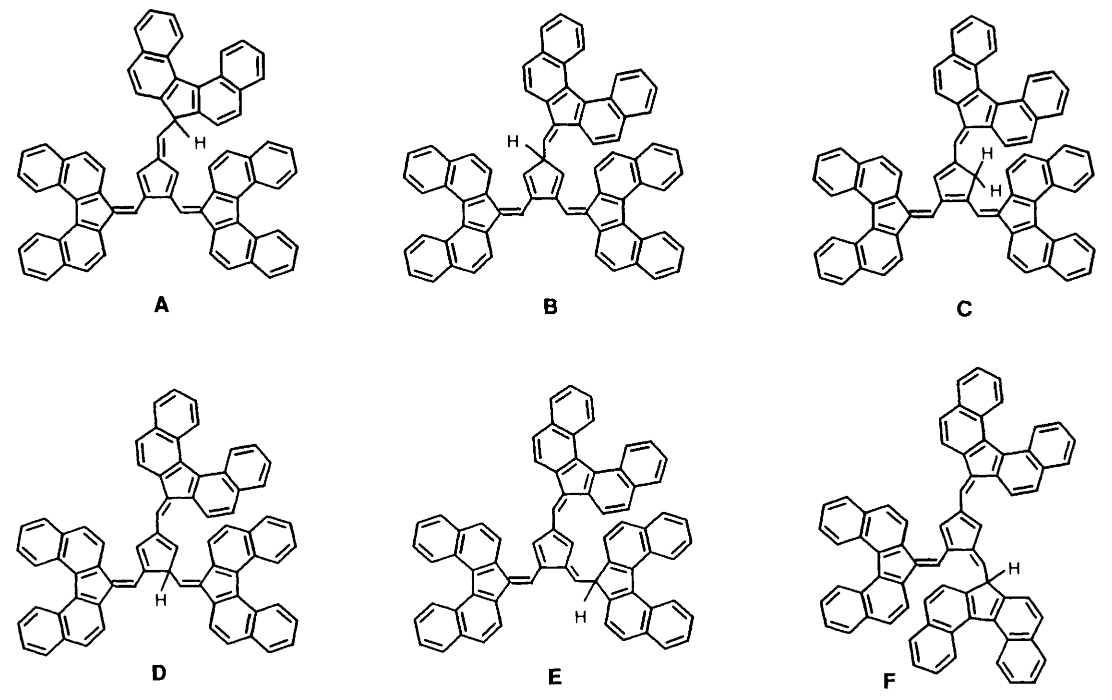


Fig. 2 Six isomers of **2a**H

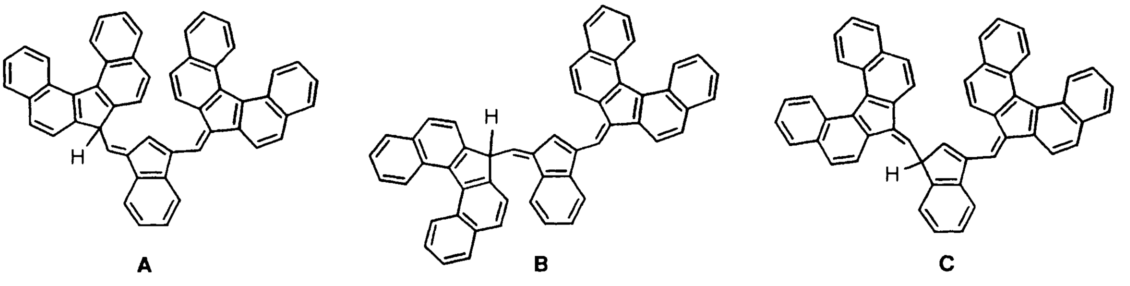


Fig. 3 Three isomers of **3a**H

E_{ox} values (kcal mol^{-1}) for the anions $\mathbf{1a}^-$, $\mathbf{2a}^-$, $\mathbf{2b}^-$, $\mathbf{3a}^-$, $\mathbf{3b}^-$ and 22 other hydrocarbon anions[6,11] including *tert*-butylcyclopentadienides[12] and the pK_a (kcal mol^{-1}) of their conjugate acids.[6,11,12] Bond dissociation energies ($E_d = 1.37pK_a + 23.1E_{ox} + 55.9$)[6,11] are almost constant, with values of 73.5, 73.1, 74.0, 72.0 and 71.4 kcal mol^{-1} for $\mathbf{1a}^-$, $\mathbf{2a}^-$, $\mathbf{2b}^-$, $\mathbf{3a}^-$ and $\mathbf{3b}^-$, respectively. The cyclic voltammograms are irreversible for $\mathbf{2a}^-$ and $\mathbf{2b}^-$ whereas those for $\mathbf{1a}^-$, $\mathbf{1b}^-$, $\mathbf{3a}^-$ and $\mathbf{3b}^-$ are reversible, indicating that the corresponding radicals to the former systems would be sufficiently unstable to undergo a coupling reaction, most probably at the C-3 position of the central cyclopentadienide ring where the steric crowding seems to be least.

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Paper 3/06642H
Received 5*th November* 1993
Accepted 22*nd November* 1993