# Stable Polycyclic Anions: Dianions from Overcrowded Ethylenes

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Stable overcrowded ethylene dianions, *viz.* bifluoren-9-ylidene dianion $(1)^{2-}$ and bi-(4*H*-cyclopenta[*def*]phenanthren-4-ylidene) dianion $(2)^{2-}$ were prepared *via* metal reduction and characterized by $^1H$ and $^{13}C$ n.m.r. spectroscopy; the spectroscopic results as well as ωβ calculations performed on the hydrocarbons (1) and (2) and the corresponding dianions $(1)^{2-}$ and $(2)^{2-}$ are discussed with respect to their diatropicity and spatial structure.

Bifluoren-9-ylidene (1) is a classical example of the family of the highly strained overcrowded ethylenes which have attracted chemists' attention in the last forty years.[1,2] The introduction of dynamic n.m.r. spectroscopy as well as other modern techniques has enabled the spatial structure of this intriguing class of compounds in solution[3,4] as well as in the solid state to be investigated in detail.[5] The parent molecule, bifluoren-9-ylidene (1) is a representative of this type of molecule and its physical properties have recently been the subject of extensive investigations.[6]

We now report the preparation and spectroscopic characterization of the stable dianions of bifluoren-9-ylidene $(1)^{2-}$ [6c] and bi-(4*H*-cyclopenta[*def*]phenanthren-4-ylidene) $(2)^{2-}$. The dianions were prepared by alkali metal reduction of the corresponding hydrocarbons in [$^2H_8$]tetrahydrofuran. The $^1H$ and $^{13}C$ parameters of the neutral as well as the charged systems are summarized in Table 1. The dianionic nature of $(1)^{2-}$ and $(2)^{2-}$ was deduced from $^1H$ and $^{13}C$ chemical shift–charge density correlations[7] and quenching experiments. The proton assignment of (2) and $(2)^{2-}$ was assisted by 2D-COSY 45 experiments.[8] A clear long-range coupling ($^4J_{HH}$) between the singlet (which is virtually an unresolved doublet) attributed to 8,8′,9,9′-H and only one of the doublets has been observed. The coupling between the band attributed to 8,8′,9,9′-H and the second doublet is a six-bond coupling and therefore this coupling cannot be observed in a 2D-COSY



(1)



(2)



(1a)



(2a)
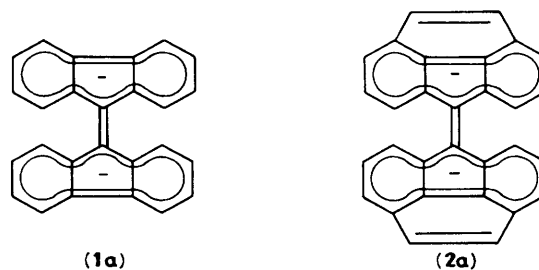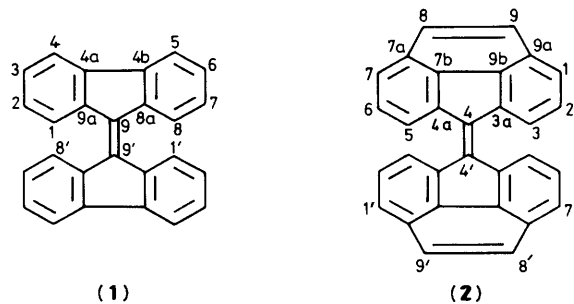
**Table 1.** $^1$H and $^{13}$C N.m.r. parameters of (1) and (2) and their correponding dianions (1)$^{2-}$ and (2)$^{2-}$.

| Compound | T/K | N.m.r. parameters[a] | Centre of gravity |
|---|---|---|---|
| (1) | 293 | $^1$H:[b] 8.46 (d, J 7.7, 1,1',8,8'), 7.85 (dd, J 7.5 and 1.0, 4,4',5,5'), 7.41 (dt, J 7.4 and 1.0, 2,2',7,7'), and 7.29 (dt, J 7.6 and 1.2, 3,3',6,6') | 7.75 |
| | 293 | $^{13}$C: 142.0, 141.4, 138.7, 129.7, 127.2, 127.0, and 120.4 | 131.6 |
| (1)$^{2-}$ 2Na$^+$ | 293 | $^1$H:[b] 8.27 (d, J 7.7, 1,1',8,8'), 7.55 (d, J 8.2, 4,4', 5,5'), 7.08 (t, J 7.2, 3,3',6,6'), and 6.70 (t, J 7.7, 2,2',7,7') | 7.40 |
| | 213 | $^1$H:[b] 8.17 (d, J 7.5, 1,1',8,8'), 7.46 (d, J 8.1, 4,4',5,5'), 6.93 (t, J 6.9, 3,3',6,6'), and 6.56 (t, J 7.3, 2,2',7,7') | 7.28 |
| | 293 | $^{13}$C: 133.1 (s), 123.1 (s), 119.7 (d), 119.3 (d), 116.7 (d), 109.0 (d), and 90.2 (s) | 117.8 |
| (2) | 293 | $^1$H:[c] 8.83 (d, J 7.7, 3,3',5,5'), 7.96 (d, J 7.5, 1,1',7,7'), 7.95 (s, 8,8',9,9'), and 7.75 (t, J 7.2, 2,2',6,6') | 8.12 |
| | 293 | $^{13}$C: 143.0, 137.2, 137.1, 128.5, 127.9, 126.0, 125.4, and 124.0 | 130.3 |
| (2)$^{2-}$ 2Na$^+$ | 293 | $^1$H:[c] 8.14 (d, J 7.7, 3,3',5,5'), 8.02 (s, 8,8',9,9'), 7.72 (t, J 7.2, 2,2',6,6'), and 7.34 (d, J 7.1, 1,1',7,7') | 7.81 |
| | 213 | $^1$H:[c] 8.00 (d, J 7.6, 3,3',5,5'), 7.94 (s, 8,8',9,9'), 7.56 (t, J 7.2, 2,2',6,6'), and 7.18 (d, J 7.0, 1,1',7,7') | 7.67 |
| | 293 | $^{13}$C: 132.5 (s), 128.4 (s), 125.5 (d), 122.9 (s), 122.4 (d), 111.5 (d), 104.9 (d), and 89.4 (s). | 119.0 |

[a] Chemical shifts are in p.p.m. downfield of SiMe$_4$ and spin–spin couplings are given in Hz. Proton assignments are given. Spectra were recorded in [$^2$H$_8$]tetrahydrofuran on a Bruker WP-200 SY spectrometer equipped with a pulse programmer and an Aspect 2000 computer operating at 200.132 and 50.32 MHz for $^1$H and $^{13}$C respectively. The field frequency regulations were maintained by $^2$H locking. [b] Assignment based on ref. 9. [c] Assignment based on 2D-COSY 45 experiments (see text).

**Table 2.** Charge density, bond length, and HOMO–LUMO energy gap of (1) and (2) and their corresponding dianions.

| Compound | Charge density[a] | Bridging bond length/Å | HOMO–LUMO[a] energy gap (β units) |
|---|---|---|---|
| (1) | 1, +0.007; 2, −0.002; 3, +0.002; 4, +0.003; 4a, −0.009; 8a, −0.014; 9, +0.028 | 1.378[a] 1.391[b] 1.377[c] 1.367[d] | 0.819 |
| (1)$^{2-}$ | 1, −0.045; 2, −0.051; 3, −0.070, 4, −0.034; 4a, −0.012; 8a, −0.094; 9, −0.188 | 1.454[a] 1.487[e] | 0.658 |
| (2) | 1, +0.004; 2, −0.002; 3, +0.010; 3a, −0.013; 4, +0.021; 7a, +0.002; 7b, −0.012; 8, +0.001 | 1.380[a] | 0.713 |
| (2)$^{2-}$ | 1, −0.078; 2, −0.048; 3, −0.054; 3a, −0.089; 4, −0.190; 7a, −0.028; 7b, −0.094; 8, −0.013 | 1.454[a] | 0.463 |

[a] Calculated values as obtained in this work by ωβ calculations, see ref. 12. Only one of the 4 (or 2) equivalent positions is numbered for brevity. [b] Calculated value obtained by Simonetta et al., ref. 13. [c] Value reported in the X-ray study in ref. 5c. [d] Value reported in the X-ray structure in ref. 5d. [e] Value reported in the X-ray structure in ref. 6c.

experiment in which long-range couplings are not emphasized. On this basis we assign the doublet which was coupled to 8,8',9,9'-H to 1,1',7,7'-H.

It was recently concluded by electrochemical studies that the reduction of (1) is reversible[4f] contrary to a previous study.[4a] We find that these dianions are very stable indeed, as they can be stored at −30 °C in an n.m.r. tube for months without any detectable decomposition.

It is well established that proton chemical shifts are sensitive to both anisotropic and charge density effects. However, the major effect which governs the carbon-13 chemical shifts of a set of sp$^2$ hybridized carbons is the charge density at the relevant carbon atom.[7c,d] The proton data in Table 1 show a small change of the centre of gravity of the signals of the dianions (1)$^{2-}$ and (2)$^{2-}$ relative to the parent compounds, contrasting with the significant shift of the centre of gravity of the carbon spectra to high field. The total carbon shifts (ΣΔδ $^{13}$C) are 358.8 p.p.m. and 338 p.p.m. for (1) → (1)$^{2-}$ and (2)

→ (2)$^{2-}$ respectively. These high-field shifts correspond to two units of charge according to carbon chemical shift–charge density correlations.[7c,d] Our observations are in line with the formation of charged diatropic species in which the high-field shift caused by the negative charge density is balanced by their diatropicity due to a 'ring current effect.'[10] The number of π electrons of (1)$^{2-}$ and (2)$^{2-}$ is 28 and 32 respectively (4nπe) and at first sight one would classify them as paratropic systems. In view of their diatropicity it seems, however, that the best representation of the corresponding dianions is given by structures (1a) and (2a) in which two conjugated circuits[11] of (4n+2)π electrons prevail.

Calculations (ωβ) were performed on (1), (2), and the corresponding dianions.[12] Calculated charge densities as well as bond lengths of the ethylene bonds and the HOMO–LUMO energy gaps are shown in Table 2. The variations of the HOMO–LUMO energy gaps as a result of the reduction process are rather small. These results are in line with the

diatropic nature of the systems[14] as depicted by structures (1a) and (2a). An interesting observation is the high charge density which resides on C-9,9' in (1) and C-4,4' in (2) (the ethylene moiety) of these dianions. The chemical shifts of these carbon atoms in (1)$^{2-}$ and (2)$^{2-}$ are $\delta$ 90.2 and 89.4 respectively (Table 1). The calculated charge densities at these positions are $-0.188$ in (1)$^{2-}$ and $-0.190$ in (2)$^{2-}$ (Table 2). The high charge density is accompanied by a drastic change of the length of the central bridging double bond.[6c] The increase in the length of the central double bond (Table 2) can be rationalized by Coulombic repulsion caused by the high charge density at each end. The weak double bond character (of the ethylene moiety) may affect the stereochemistry of these charged systems, as compared to the highly strained hydrocarbons. A most interesting characteristic of this type of hydrocarbon (1) and (2) is their spatial structure. In principle two structures are possible: a doubly folded (A form) or a twisted one (B form). In solution, (1) is believed to exist in the twisted form (B form).[3b,4f] The fact that in the dianions the bond order of the central bond is decreased considerably suggests that in the dianions the activation energy for rotation about the 'double' bond should be rather low.[15]

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