# The Radical Anion of 1,8-Diphenylnaphthalene: Re-examination of E.S.R. and ENDOR Spectra

**Fabian Gerson,* René Heckendorn, and Reinhart Möckel**
*Institut für Physikalische Chemie der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland*

At variance with the statement made in a previous paper, the bulk of the π-spin population in the radical anions of 1,8-diphenyl- and 1,8-bis(tolyl)-naphthalene is located in the naphthalene moiety.

Three years ago, the results of an ENDOR study were reported for the radical anions of 1,8-diphenyl- (**1**), 1,8-bis(perdeuteriophenyl)- $[^2H_{10}]$-(**1**), and 1,8-bis(*p*-tolyl)-naphthalene (**2**).[1] The authors concluded that the π-spin population in these radical anions is markedly shifted from the naphthalene moiety to the phenyl substituents, owing to the transannular 'paracyclophane-like' interaction between the benzene rings which renders their LUMO comparable in energy to the LUMO of naphthalene. This conclusion, which we now show is erroneous, was quoted twice in a recent review.[2]

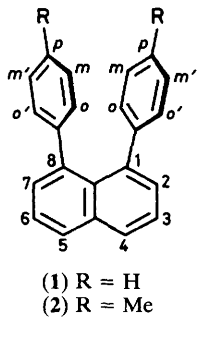
We have re-examined the e.s.r. and ENDOR spectra of the radical anions $(\mathbf{1}^{\cdot-})$, $[^2H_{10}]$-$(\mathbf{1}^{\cdot-})$, and $(\mathbf{2}^{\cdot-})$. In Table 1, the hyperfine data obtained in this work are compared with those reported for $(\mathbf{1}^{\cdot-})$ and $(\mathbf{2}^{\cdot-})$ in the literature.[1] The striking differences between the two sets of data originate from the previous failing to observe the ENDOR signals associated with the largest proton coupling constant (4,5-positions). The revised values are consistent with the bulk of the π-spin population being located in the naphthalene moiety, as anticipated from the substantially less negative half-wave reduction potential of naphthalene ($E_{1/2}$ −2.5 V *vs.* standard calomel electrode) relative to [2.2]paracyclophane ($E_{1/2}$ −3.0 V).[3] The corresponding potential of (**1**) ($E_{1/2}$ −2.3 V) complies with the expected effect of diphenyl-substitution on the naphthalene π-system.

Further reduction of $(\mathbf{1}^{\cdot-})$, $[^2H_{10}]$-$(\mathbf{1}^{\cdot-})$, and $(\mathbf{2}^{\cdot-})$ leads to the dianions $(\mathbf{1}^{2-})$, $[^2H_{10}]$-$(\mathbf{1}^{2-})$, and $(\mathbf{2}^{2-})$ and subsequently to the radical trianions $(\mathbf{1}^{\cdot 3-})$, $[^2H_{10}]$-$(\mathbf{1}^{\cdot 3-})$, and $(\mathbf{2}^{\cdot 3-})$. It is noteworthy that in these trianions the π-spin population resides mainly in the phenyl substituents. A full account of the e.s.r. and ENDOR studies on the radical anions and trianions of (**1**), $[^2H_{10}]$-(**1**), and (**2**) will be given elsewhere,[4] along with the results of the analogous investigations on derivatives bridged in the *para*-positions.

**Table 1.** Proton coupling constants, in mT, for the radical anions $(\mathbf{1}^{\cdot-})$ and $(\mathbf{2}^{\cdot-})$.[a] The values in parentheses are those of ref. 1.

| Position | $(\mathbf{1}^{\cdot-})$ | $(\mathbf{2}^{\cdot-})$ |
|---|---|---|
| 2,7 | 0.261 (0.059) | 0.250 (0.056) |
| 3,6 | 0.060 (0.059) | 0.070[d] (0.056) |
| 4,5 | 0.459 (0.263) | 0.456 (0.250) |
| *o,o′* | 0.096[b] (0.096)[c] | 0.098 (0.100)[c] |
| | 0.057[b] (0.059)[c] | 0.057[d] (0.070)[c] |
| *m,m′* | 0.035[b] (0.034)[c] | 0.034 (0.033)[c] |
| | 0.019[b] (0.018)[c] | 0.025 (0.026)[c] |
| *p* | 0.114[b] (0.115) | 0.113[e] (0.112) |

[a] Solvent: 1,2-dimethoxyethane; counterion: $K^+$; temperature: 193 K. Experimental error: ±0.001 mT. [b] Replaced by deuteron coupling constants in the spectra of $[^2H_{10}]$-$(\mathbf{1}^{\cdot-})$. [c] Not assigned in ref. 1. [d] Assignment uncertain; may be reversed. [e] Coupling constant of the six methyl protons.



(**1**) R = H
(**2**) R = Me

This work was supported by the Swiss National Science Foundation.

*Received, 2nd January 1985; Com. 005*

## References

1 F. Nemoto, A. Takaoka, and K. Ishizu, *Chem. Phys. Lett.*, 1982, **86**, 401.
2 'Electron Spin Resonance,' (Specialist Periodical Report), Royal Society of Chemistry, 1983, Vol. 8, Ch. 4, p. 74 and Ch. 8, p. 295.
3 F. Gerson, H. Ohya-Nishiguchi, and Ch. Wydler, *Angew. Chem.*, 1976, **88**, 617; *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 552; R. Jund, P. Lemoine, and M. Gross, *Angew. Chem.*, 1982, **94**, 312; *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 305.
4 F. Gerson, R. Heckendorn, R. Möckel, and F. Vögtle, *Helv. Chim. Acta*, to be published.