

Novel Chemical Species: Radical Trianions

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Organic molecules accommodating one or several additional negative charges not only provide another testing ground for theoretical and structural studies but also represent novel species for synthetic applications. The radical anions of unsaturated compounds have been thoroughly investigated by ESR spectroscopy for several decades,¹ and their relevance to chemical reactions is now well documented.^{2,3} Likewise, a number of corresponding dianions have been characterized by their NMR spectra,⁴ and some of them proved to be useful as precursors of hitherto unknown products.^{3,5} By contrast, full evidence of higher negatively charged species was virtually lacking until a few years ago. In previously published isolated reports, formation of radical trianions was suggested by the appearance of new ESR spectra on prolonged reduction,⁶ but in none of these cases⁷⁻¹¹ has the identity of the species in question been unequivocally confirmed by the analysis of their hyperfine structure. The present paper is a brief review of recent, more systematic studies on the radical trianions of conjugated π -systems. It considers the theoretical requirements and the experimental conditions for the generation of these highly charged species, and it discusses the structural information acquired from their ESR and ENDOR spectra. The detection and characterization of radical trianions would be of great interest if merely for the esoteric nature of three negative charges confined in a restricted space of a single molecule. Even more so, since as will be shown below, these species strongly differ in their electronic structure from the corresponding radical anions and dianions, and thus they may pave new routes as starting materials and intermediates in organic synthesis.

When Are Radical Trianions Expected To Form?

The ease of formation of a radical trianion, X^{3-} , in solution is determined by (i) the energy level of the next lowest unoccupied molecular orbital (NLUMO) in the corresponding neutral compound X, (ii) the electrostatic repulsion energy of the three negative charges, and (iii) the association of X^{3-} with its three positively charged counterions M^+ .

(i) Availability of a low-lying NLUMO is essential for the uptake of a third additional electron by the compound, since the LUMO has been filled by accommodating the two extra electrons in the dianion X^{2-} .¹² A

NLUMO of such an energy may be indicated theoretically by MO models and/or experimentally by polarography or cyclic voltammetry.¹³ Compounds which meet this criterion for the NLUMO and therefore represent promising candidates for radical trianions are non-benzenoid unsaturated hydrocarbons of substantial size, like nonalternant polycyclic π -systems or derivatives of larger annulenes.

(ii) An extended molecular framework is a prerequisite for reducing the electrostatic repulsion energy of three negative charges. In this respect, compounds embodying several electron acceptor sites are favored; such a site can be either a conjugated hydrocarbon or a substituent containing heteroatoms.

(iii) In solution, tight association with three counterions M^+ promotes formation of the radical trianion, since, in general, electrostatic attraction between the oppositely charged ions stabilizes X^{3-} more strongly than the dianion X^{2-} and the radical anion $X^{\bullet-}$.

How Are Radical Trianions Generated?

Imposing three negative charges on a compound requires powerful reducing agents, so that reaction with an alkali metal is the standard procedure for preparation of the radical trianions. The most convenient reagent is potassium in 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), or 2-methyltetrahydrofuran (MTHF). Admixture of a solvent which loosens the association between X^{3-} and its counterions M^+ , like

(1) See, e.g.: de Boer, E.; Weissman, S. I. *J. Am. Chem. Soc.* 1958, 80, 4549. Carrington, A. *Q. Rev. Chem. Soc.* 1963, 17, 67. *Radical Ions*; Kaiser, E. T., Kevan, L., Eds.; Wiley-Interscience: New York, 1968. Gerson, F. *High-Resolution ESR Spectroscopy*; Verlag Chemie and Wiley: Weinheim (FRG) and New York, 1970.

(2) See, e.g.: Birch, A. J.; Subba Rao, G. *Adv. Org. Chem.* 1972, 8, 1. Kornblum, N.; Boyd, S. D.; Ono, N. *J. Am. Chem. Soc.* 1974, 96, 2580. Russell, G. A.; Schmitt, K. D.; Mattox, J. *Ibid.* 1975, 97, 1882. Maruyama, K.; Katagiri, M. *Ibid.* 1986, 108, 6263. Ashby, E. C. *Pure Appl. Chem.* 1980, 52, 545.

(3) Holy, N. L. *Chem. Rev.* 1974, 74, 243.

(4) See, e.g.: Lawler, R. G.; Ristagno, C. V. *J. Am. Chem. Soc.* 1969, 91, 1534. Oth, J. F. M.; Baumann, H.; Gilles, J.-M.; Schröder, G. *Ibid.* 1972, 94, 3498. Oth, J. F. M.; Woo, E. P.; Sondheimer, F. *Ibid.* 1973, 95, 7337. Müllen, K. *Helv. Chim. Acta* 1978, 61, 2307.

(5) See, e.g.: Vogel, E.; Engels, H.-W.; Huber, W.; Lex, J.; Müllen, K. *J. Am. Chem. Soc.* 1982, 104, 3729. Huber, W.; Lex, J.; Meul, T.; Müllen, K. *Angew. Chem.* 1981, 93, 401; *Angew. Chem., Int. Ed. Engl.* 1981, 20, 391.

(6) Radical trianions were supposed to be formed of 9,10-dioxophenanthrene,⁷ 2,4,6-triphenyl- λ^3 -phosphorin,⁸ oxalic acid,⁹ tri-naphthylene,⁹ heptafulvalene,¹⁰ and [6]helicene.¹¹

(7) Bauld, N. L. *J. Am. Chem. Soc.* 1964, 86, 3894.

(8) Dimroth, K.; Steuber, F. W. *Angew. Chem.* 1967, 79, 410; *Angew. Chem., Int. Ed. Engl.* 1967, 6, 446.

(9) Sommerdijk, J. L.; de Boer, E.; Pijpers, F. W.; van Villigen, H. Z. *Phys. Chem. (Munich)* 1969, 63, 183.

(10) Bauld, N. L.; Chang, C.-S.; Eilert, J. H. *Tetrahedron Lett.* 1973, 153.

(11) Weissman, S. I.; Chang, R. J. *J. Am. Chem. Soc.* 1972, 94, 8683. Fey, H. J.; Kurreck, H.; Lubitz, W. *Tetrahedron* 1979, 35, 905.

(12) The LUMO and NLUMO nomenclature refers to the orbital occupancies in the neutral compound X.

(13) For a review on cyclic voltammetry see: Heinze, J. *Angew. Chem.* 1984, 96, 823; *Angew. Chem., Int. Ed. Engl.* 1984, 23, 831.

Fabian Gerson was born in Poland in 1928. He studied natural sciences at the ETH Zürich, Switzerland, where he received a D.Sc. degree in 1958. Since 1968 he has held a professorship in physical chemistry at the University of Basel. His main research interests are in ESR spectroscopy of π -radical ions in which field he has published most of his 150 papers, a textbook, and a few review articles.

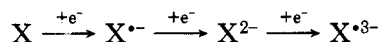
Walter Huber was born in Switzerland in 1949. He studied chemistry at the University of Basel where he received his Ph.D. in 1979. After 2 post-doctoral years with K. Müllen at the University of Köln, he returned to Basel as a research assistant. He was appointed Privatdozent in 1986. His work is mainly concerned with NMR and ESR spectra of highly charged π -electron species.

hexamethylphosphoric triamide (HMPT), has usually been found disadvantageous. In some cases,¹⁴ radical trianions could also be generated by electrolytic reduction, provided that the conventional polar solvent, such as *N,N*-dimethylformamide (DMF), MeCN, or Me₂SO, had been replaced by DME or THF. Occasionally, when the compound X was not readily accessible, the dianion X²⁻ produced from a suitable dihydro precursor XH₂ served as the starting material.¹⁴

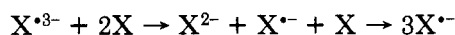
It goes without saying that reduction of a neutral compound X to its trianion X³⁻ is more demanding than its conversion to less negatively charged ions, although the general procedures are essentially the same. The reaction time is much longer and the purity requirements are more stringent than for preparation of X⁻. In particular, even traces of protic impurities can give rise to the radical anion of a dihydro derivative (XH₂), instead of X³⁻, as a final product.¹⁵ Side reactions, in which the molecular framework of X is altered, should be restrained by keeping the solution at low temperatures during the reduction process.

In What Way Can the Identity of Radical Trianions Be Proved?

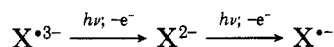
The first indication that the radical trianion X³⁻ has been formed is provided by the sequence of the reduction steps, as monitored by ESR spectroscopy. This sequence



is revealed by (i) the spectrum of the radical anion X^{·-}, (ii) its disappearance due to the formation of the dianion X²⁻, and (iii) the emergence of a new spectrum ascribed to X³⁻. In order to certify that the new ESR spectrum does, in fact, arise from the radical trianion and not from a secondary paramagnetic product, experiments should be performed by which X³⁻ is reoxidized to X^{·-}. This reaction can be brought about by comproportionation



and/or by irradiation



It is manifested by the ESR spectrum of X^{·-} superseding that of X³⁻.

The most convincing argument in favor of the radical trianion X³⁻ as the finally obtained paramagnetic species is the structural information derived from the hyperfine data. Not only do these data define the symmetry of a radical and the number of its interacting nuclei, but they are also related to the spin distribution predicted by MO models. The data acquisition presupposes, however, a reliable analysis of the ESR spectrum. In the case of X³⁻, such an analysis is often impeded by line broadening which results from unresolved hyperfine splittings due to the nuclei of the counterions M⁺¹⁶ and/or from an electron exchange

(14) Gerson, F.; Heckendorn, R.; Cowan, D. O.; Kini, A. M.; Maxfield, M. *J. Am. Chem. Soc.* **1983**, *105*, 7017.

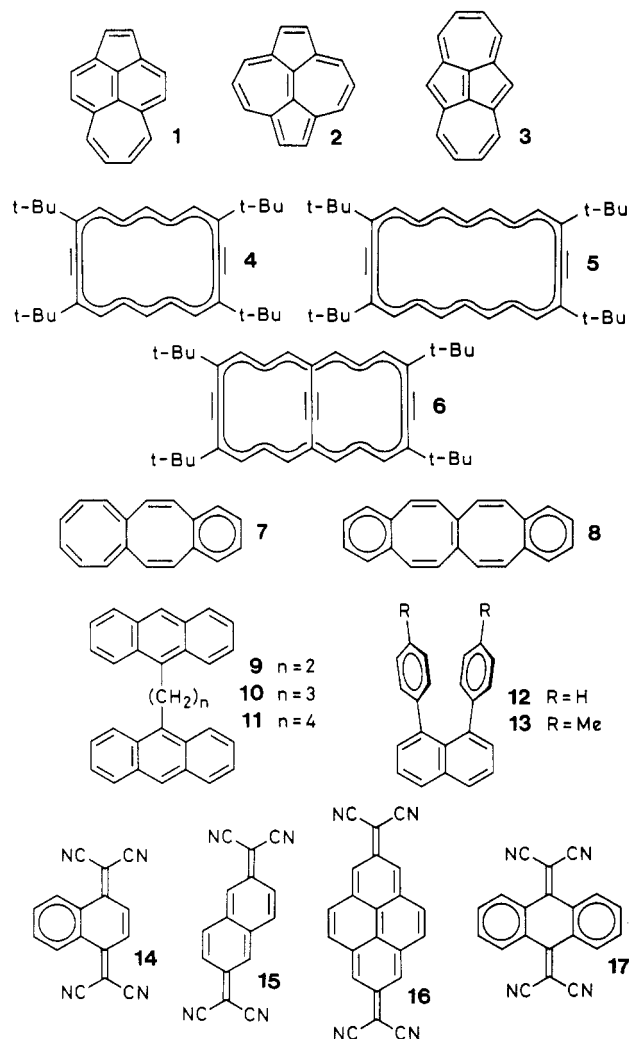
(15) Schnieders, C.; Müllen, K.; Huber, W. *Tetrahedron* **1984**, *40*, 1701.

(16) Despite the anticipated strong association of the radical trianions with their three positively charged counterions, hyperfine splittings from alkali-metal nuclei (⁷Li, ²³Na, ³⁹K, or ¹³³Cs) in these counterions are generally too small to be resolved in the ESR spectra. The reason for that finding is not yet fully understood.

with diamagnetic species (dianions X²⁻ and tetraanions X⁴⁻). Fortunately, unless the exchange excessively shortens the electron relaxation times, this handicap can be overcome by the use of electron nuclear double resonance (ENDOR). The ENDOR technique enables one to determine the hyperfine coupling constants (hfc's), even when overlapping lines make the ESR spectrum too complex or too poorly resolved for a direct analysis.¹⁷

Which Radical Trianions Have Been Identified?

The compounds, of which the radical trianions have so far been characterized by ESR and ENDOR spectroscopy, are represented by formulas 1–16.



These compounds can be classified as follows (the references are concerned with their syntheses): (i) non-alternant isopyrenes 1,¹⁸ 2,¹⁹ and 3;²⁰ (ii) bisdehydro-[*n*]annulenes 4²¹ and 5,²² including the analogous

(17) For applications of ENDOR spectroscopy see: Kurreck, H.; Kirste, B.; Lubitz, W. *Angew. Chem.* **1984**, *96*, 171; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 173.

(18) Boekelheide, V.; Vick, G. K. *J. Am. Chem. Soc.* **1956**, *78*, 653.

(19) Anderson, A. G., Jr.; MacDonald, A. A.; Montana, A. F. *J. Am. Chem. Soc.* **1968**, *90*, 2993. Jutz, Ch.; Schweiger, E. *Synthesis* **1974**, 193.

(20) Reel, H.; Vogel, E. *Angew. Chem.* **1972**, *84*, 1064; *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1013.

(21) Iyoda, M.; Nakagawa, M. *Tetrahedron Lett.* **1972**, 3161.

(22) Iyoda, M.; Nakagawa, M. *J. Chem. Soc., Chem. Commun.* **1972**, 1003.

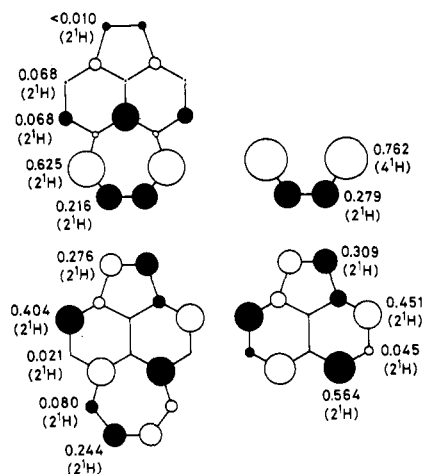


Figure 1. Top: NLUMO of acepleiadylene (1) and hfcc's for 1^{3-} compared with LUMO of 1,3-butadiene and hfcc's for the radical anion of its (E) isomer.³⁶ Bottom: LUMO of 1 and hfcc's for 1^{-} compared with LUMO of acenaphthylene and hfcc's for its radical anion.³⁷ All values in mT. Assignments of hfcc's for 1^{-} differ somewhat from the previous ones.^{34,35}

[14]annuleno[14]annulene 6;²³ (iii) benzo (7) and dibenzo (8) derivatives^{24,25} of octalene;²⁶ (iv) α,ω -dianthrylalkanes 9, 10, and 11;²⁷ (v) 1,8-diphenyl-naphthalenes 12 and 13;^{28,29} and (vi) tetracyanoarenoquinodimethanes 14,³⁰ 15,³¹ and 16.³²

Nonalternant Isopyrenes. The Hückel energies, $\alpha + x\beta$, of the NLUMO's in acepleiadylene (cyclohept[fg]acenaphthylene; 1), bicyclopenta[ef,kl]heptalene (2), and bicyclohepta[cd,gh]pentalene (3) are rather close to those of the LUMO's, and they exhibit relatively low $|x|$ values.

	x		
	1	2	3
NLUMO	-0.503	-0.445	-0.479
LUMO	-0.445	-0.362	-0.445

The hfcc's of the protons in the radical trianions 1^{3-} ^{33,34} and 2^{3-} ³⁴ are consistent with the single occupancies of the NLUMO's, as illustrated for 1^{3-} in Figure 1. It is evident therefrom that the π -spin population in 1^{3-} is to a large extent localized on the butadiene moiety, whereas in the corresponding radical anion 1^{-} ^{34,35} it resides mainly at the acenaphthylene part of the π -system. For 3^{3-} ^{33,34} the interpretation of the hyperfine data is complicated by the association of the radical trianion with its three alkali-metal counterions M^+ . The

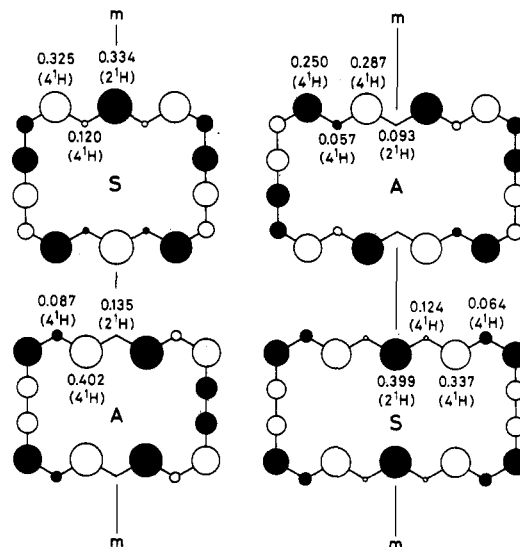


Figure 2. Lowest antibonding π -perimeter orbitals as models for LUMO's and NLUMO's of bisdehydro[n]annulenes 4 ($n = 18$) and 5 ($n = 22$): top left, NLUMO of 4 and hfcc's for 4^{3-} ; top right, NLUMO of 5 and hfcc's for 5^{3-} ; bottom left, LUMO of 4 and hfcc's for 4^{-} ; bottom right, LUMO of 5 and hfcc's for 5^{-} . All values in mT.

ion pairing lowers the D_{2h} symmetry of 3^{3-} and makes the energetic sequence of the orbitals in the radical trianion dependent on the nature of M . While, with $M = \text{Li}$, it is expectedly the NLUMO that houses the unpaired electron, an orbital resembling the LUMO¹² becomes singly occupied when $M = \text{Na}$ or K .³⁴ Obviously, the tightening of the association between 3^{3-} and its counterions M^+ with the increasing size of M ³⁸ is sufficient to shift the energy of the LUMO above that of the NLUMO, since the two orbitals are separated in 3 by only a small energy gap (0.034β). This "orbital switch" can be simulated within the Hückel model by applying the " ω -technique"⁴⁰ to 3^{3-} .

In contrast to the ESR spectra of other radical trianions dealt with in the present review,¹⁶ those of 1^{3-} and 3^{3-} usually exhibit resolved hyperfine splittings from the nuclei of alkali-metal counterions. It is noteworthy that these splittings are due to *two* equivalent ²³Na or ³⁹K nuclei, which means that two out of three counterions tightly associate with 1^{3-} and 3^{3-} . Presumably, the two cations are situated in equivalent positions on each side of the molecular plane and in the proximity of the radical trianion, whereas the third cation is located in a more distant site.

Bisdehydro[n]annulenes. For an unperturbed n -membered π -perimeter of $n = 4N + 2$ centers ($N = 1, 2, \dots$) and D_{nh} symmetry, the lowest antibonding orbitals are doubly degenerate. The degeneracy is removed in the tetra-*tert*-butylbisdehydro[n]annulenes 4 ($n = 18$) and 5 ($n = 22$), but the LUMO and NLUMO correlating with these perimeter orbitals remain energetically close to each other and can accommodate up

(23) Akiyama, S.; Iyoda, M.; Nakagawa, M. *J. Am. Chem. Soc.* 1976, 98, 6410.

(24) Breslow, R.; Horspool, W.; Sugiyama, H.; Vitale, W. *J. Am. Chem. Soc.* 1966, 88, 3677.

(25) Engels, H.-W. Dissertation, Universität Köln, 1980.

(26) Vogel, E.; Runzheimer, H.-V.; Hogrefe, F.; Baasner, B.; Lex, J. *Angew. Chem.* 1977, 89, 909; *Angew. Chem., Int. Ed. Engl.* 1977, 16, 871.

(27) De Barry Barnet, E.; Matthews, M. A. *Chem. Ber.* 1926, 59, 767.

(28) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* 1972, 37, 1003.

(29) Clough, R. L.; Mison, P.; Roberts, J. D. *J. Org. Chem.* 1976, 41, 2252.

(30) Chatterjee, S. *J. Chem. Soc. B* 1967, 1170.

(31) Sandman, D. J.; Garito, A. F. *J. Org. Chem.* 1974, 39, 1165.

(32) Maxfield, M.; Willi, S. M.; Cowan, D. O.; Bloch, A. N.; Pöehler, T. O. *J. Chem. Soc., Chem. Commun.* 1980, 947.

(33) Huber, W. *Tetrahedron Lett.* 1983, 3595.

(34) Huber, W. *Helv. Chim. Acta* 1983, 66, 2582.

(35) Gerson, F.; Heinzer, J. *J. Chem. Soc., Chem. Commun.* 1965, 488; *Helv. Chim. Acta* 1966, 49, 7.

(36) Myers, R. J.; Levy, D. H. *J. Chem. Phys.* 1964, 41, 1062.

(37) Gerson, F.; Weidmann, B. *Helv. Chim. Acta* 1966, 49, 1837.

(38) Such a tightening of the association with the alkali-metal counterions has been observed for aromatic radical anions in ethereal solvents.³⁹ It is due to the decreasing solvation of the cation in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.

(39) See, e.g.: Buschow, K. H. J.; Dieleman, J.; Hoijsink, G. *J. J. Chem. Phys.* 1965, 42, 1993.

(40) Streitwieser, A. J., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; p 115.

to four electrons.⁴¹ The relevant degenerate orbitals of the 18- and 22-membered perimeters (Hückel-MO energies $\alpha - 0.347\beta$ and $\alpha - 0.285\beta$, respectively) are depicted in Figure 2, whereby the perimeters have been drawn in the shape of the carbon frameworks in the corresponding bisdehydro[*n*]annulenes 4 and 5. An orbital belonging to a degenerate pair is classified as symmetric (S) or antisymmetric (A) with respect to a mirror plane (m) passing through two opposite centers and perpendicular to the plane of the perimeter. Introduction of the two triple bonds into the cyclic π -system of 4 destabilizes the S orbital and stabilizes its A counterpart, whereas a reverse energy sequence of the perimeter S and A orbitals is obtained by applying an analogous perturbation treatment to 5. As shown in Figure 2, the ¹H hfcc's for the radical anions 4^{•-} and 5^{•-}^{42,43} and for the radical trianions 4^{•3-} and 5^{•3-}⁴³ reflect the nodal properties predicted for the LUMO's and NLUMO's; the values for the two equivalent protons in the mirror plane m are most diagnostic in this respect.

Interestingly, the ¹H hfcc's for the radical anion and the radical trianion of the tetra-*tert*-butyltrisdehydro-[22]bi[10.10.2]annulene (6)⁴⁴ strongly resemble the corresponding values for 5^{•-} and 5^{•3-}. This finding indicates that the π -spin distribution over the 22 carbon atoms of the peripheral ring in 6^{•-} and 6^{•3-} follows essentially the same pattern as in 5^{•-} and 5^{•3-}, respectively, notwithstanding the presence of the bridging acetylenic group.

Benzo and Dibenzo Derivatives of Octalene. The physical and chemical properties of octalene,²⁶ a non-planar molecule of olefinic character, are similar to those of the structurally related cyclooctatetraene.⁴⁵ Accordingly, octalene is readily converted to its dianion and, subsequently, to its tetraanion,⁴⁶ in which the carbon framework is flattened and the C-C bond lengths are largely equalized. As in the case of the cyclooctatetraene radical anion, the intermediately formed paramagnetic species are prone to disproportionation, so that the ESR spectrum of the octalene radical anion could be observed solely in polar solvents; the corresponding radical trianion has so far escaped detection.⁴⁷ Benzo annelation of octalene not only make the uptake of additional electrons more difficult but also causes the disproportionation of the radical trianion to the dianion and tetraanion to become less pronounced. Thus, for benzo[*c*]octalene (7)⁴⁷ and dibenzo[*c,j*]octalene (8),^{33,47} both the radical anions and the radical trianions have been fully characterized by their hyperfine data. These values are in essential agreement with the spin distribution predicted for planar delocalized π -systems.

α,ω -Dianthrylalkanes. Each of the two 9-anthryl moieties, which are linked by two (9), three (10), or four methylene groups (11), can take up two additional

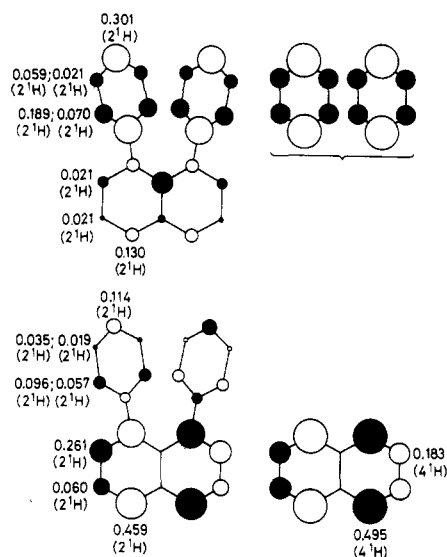


Figure 3. Top: NLUMO of 1,8-diphenylnaphthalene (12) and hfcc's for 12^{•3-} compared with a combination of two "symmetric" lowest antibonding benzene MO's. Bottom: LUMO of 12 and hfcc's for 12^{•-} compared with the LUMO of naphthalene and hfcc's for its radical anion.⁵² All values in mT. Additional HMO parameters for 12: $\beta_{C(Ph)-C(naphthalene)} = 0.7\beta$.

electrons to yield the corresponding tetraanions,⁴⁸ intermediately, the radical anions, the dianions, and the radical trianions are formed.^{33,48} The frequency of electron transfer between the two anthryl moieties is determined by the rate of the simultaneously occurring migration of the counterions M⁺. In the radical anions 9^{•-}, 10^{•-}, and 11^{•-} with M = K, this motion is slow on the hyperfine time scale when the solvent is MTHF, but it becomes fast in a mixture of DME and HMPT.⁴⁸ ESR signals due to the triplet state are detected for the dianion; the observed zero-field splitting parameters of 8.4 (9²⁻), 5.5 (10²⁻), and 3.5 mT (11²⁻) are consistent with each anthracene π -system accommodating one unpaired electron.⁴⁸ Conversion of the dianions into the corresponding radical trianions can be conceived as the admission of an extra electron into one of the π -systems, thus giving rise to a diamagnetic anthracene dianion linked by the polymethylene chain to an anthracene radical anion. Such a model accounts, in fact, for the ESR and ENDOR spectra of 9^{•3-}, 10^{•3-}, and 11^{•3-}. The electron transfer between the two anthryl moieties in these radical trianions is slow on the hyperfine time scale irrespective of the solvent used, and the hfcc's of the aromatic protons are similar to those for the radical anion of 9-methylanthracene.⁴⁹

1,8-Diphenylnaphthalenes. The phenyl substituents in 1,8-diphenylnaphthalene (12) are twisted out of planarity with the naphthalene π -system, thus assuming a cyclophane-like geometry.²⁸ Compound 12 can, therefore, be regarded as embracing both the naphthalene and the cyclophane substructures. As demonstrated in Figure 3, the LUMO of 12 closely resembles the corresponding orbital of naphthalene, aside from partial delocalization into the two phenyl substituents. On the other hand, the NLUMO of 12 represents a combination of two "symmetric" lowest antibonding

(41) Müllen, K.; Huber, W.; Meul, T.; Nakagawa, M.; Iyoda, M. *J. Am. Chem. Soc.* **1982**, *104*, 5403.

(42) Gerson, F.; Jachimowicz, J.; Nakagawa, M.; Iyoda, M. *Helv. Chim. Acta* **1974**, *57*, 2141.

(43) Huber, W. *Helv. Chim. Acta* **1985**, *68*, 1140.

(44) Huber, W.; Müllen, K.; Schnieders, C.; Iyoda, M.; Nakagawa, M. *Helv. Chim. Acta* **1986**, *69*, 949.

(45) Fray, G. I.; Saxton, R. *The Chemistry of Cyclooctatetraene and Its Derivatives*; Cambridge University Press: London, 1978.

(46) Müllen, K.; Oth, J. F. M.; Engels, H.-W.; Vogel, E. *Angew. Chem.* **1979**, *91*, 251; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 229.

(47) Huber, W. Habilitationsschrift, Universität Basel, 1985.

(48) Huber, W.; Unterberg, H.; Müllen, K. *Angew. Chem.* **1983**, *95*, 239; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 242.

(49) Bolton, J. R.; Carrington, A.; McLachlan, A. D. *Mol. Phys.* **1962**, *5*, 31.

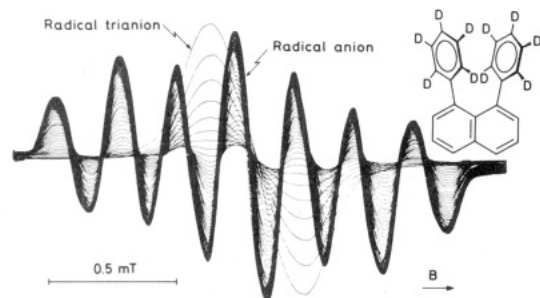


Figure 4. ESR spectra observed upon photooxidation of $12\text{-}d_{10}^{3-}$ in DME at 193 K. The consecutive curves are recorded in time intervals of ca. 1 min. From ref 51.

benzene MO's with some admixture of the third lowest unoccupied orbital of naphthalene. The predictions of MO models are borne out by the hyperfine data for the radical anions^{50,51} and the radical trianions⁵¹ of **12** (Figure 3) and its derivatives in which the phenyl substituents are perdeuteriated ($12\text{-}d_{10}$) or methylated in the para positions (**13**). While the ^1H hfcc's for 12^{3-} , $12\text{-}d_{10}^{3-}$, and 13^{3-} agree with those expected for the radical anion of naphthalene slightly perturbed by two 1,8-substituents, the corresponding values for 12^{3-} , $12\text{-}d_{10}^{3-}$, and 13^{3-} are best interpreted in terms of an "open-chain" cyclophane radical anion which is attached to a naphthalene π -system bearing two negative charges.

As stated in a preceding section, radical trianions can be photooxidized to the dianions and, subsequently, to the radical anions. A nice illustration of this reaction is presented in Figure 4 which displays the ESR spectra observed upon irradiating a solution of $12\text{-}d_{10}^{3-}$ with a high-pressure Hg lamp (wavelengths < 330 nm cut off by a Pyrex filter). The gradual conversion of $12\text{-}d_{10}^{3-}$ into $12\text{-}d_{10}^{2-}$ is easily followed for these deuteriated species, owing to the apparent simplicity of their hyperfine patterns.

Tetracyanoarenoquinodimethanes. The first member in this class of electron acceptors is the tetracyano-1,4-benzoquinodimethane (TCNQ) which has become known for its salts and charge-transfer complexes exhibiting high electrical conductivity ("organic metals").⁵³ TCNQ is easily reduced to the radical anion and, under more rigorous conditions, to the dianion.⁵⁴ Extension of the benzo to a larger areno π -system makes the uptake of a third electron possible. Thus, the radical trianions of tetracyano-1,4-naphthoquinodimethane (**14**) and its 2,6-isomer (**15**) as well as that of tetracyano-2,7-pyrenoquinodimethane (**16**) have been prepared either directly from the neutral compound (**14**) or from the dianions (15^{2-} and 16^{2-}) obtained by deprotonation of dimalononitrile precursors (15H_2 and 16H_2).¹⁴ The ^1H hfcc's for 14^{3-} , 15^{3-} , and 16^{3-} strongly resemble the analogous values for the radical anions of 1,4- and 2,6-dimethylnaphthalenes⁵² and of 2,7-dimethylpyrene,⁵⁵ respectively. (The ^{14}N hfcc's from the

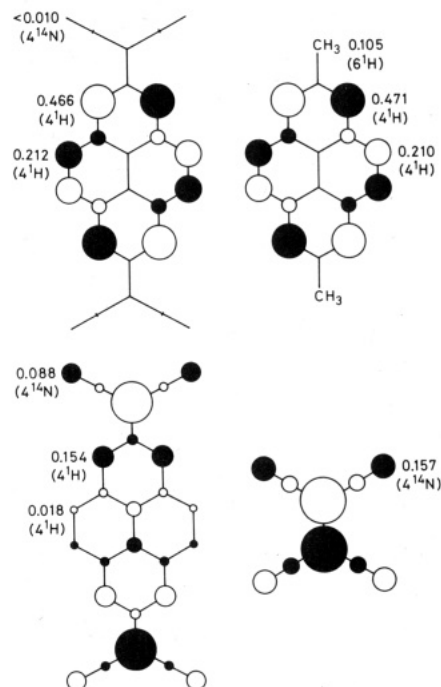


Figure 5. Top: NLUMO of tetracyano-2,7-pyrenoquinodimethane (**16**) and hfcc's for 16^{3-} compared with LUMO of pyrene and hfcc's for the radical anion of its 2,7-dimethyl derivative.⁵⁵ Bottom: LUMO of **16** and hfcc's for 16^{3-} compared with LUMO of tetracyanoethene and hfcc's for its radical anion.⁵⁸ All values in mT. Additional HMO parameters for **16** and tetracyanoethene: $\alpha_{\text{N}} = \alpha + \beta$; $\beta_{\text{C}=\text{N}} = 2\beta$; $\beta_{\text{C}-\text{CN}} = 0.9\beta$.

ciano substituents are less than the ESR line widths.) As will be shown below and as is exemplified by Figure 5 for **16**, these findings are readily rationalized in terms of a simple MO model.

A prominent feature of the LUMO's in all tetracyanoarenoquinodimethanes is the large size of the coefficients at the exocyclic carbon atoms bearing the cyano substituents (Figure 5). Taking into account the partial π -charge delocalization into these substituents, one may adequately describe the radical anions of tetracyanoarenoquinodimethanes by a structure formula which assigns a half electron spin or a half negative charge to either $\text{C}(\text{CN})_2$ group. In the dianions, each of the two groups accommodates one electron, so that another additional electron should be located in the residual areno π -system. This argumentation is in perfect accordance with the coefficients of the NLUMO's which mimic the LUMO's of the corresponding aromatic hydrocarbons and which vanish or are very small at the $\text{C}(\text{CN})_2$ groups. As demonstrated for 16^{3-} in Figure 5, the radical trianions of tetracyanoarenoquinodimethanes can thus be regarded as the radical anions of these hydrocarbons substituted by two negatively charged $\text{C}(\text{CN})_2$ groups.

Since the bulk of the π -spin population in 16^{3-} resides at the exocyclic carbon atoms that are void of protons, the hfcc's for 16^{3-} , like those for the radical anions of other tetracyanoarenoquinodimethanes, are relatively small (Figure 5). The ESR spectrum of 16^{3-} has therefore a total width of only 1.4 mT, as compared to the analogous value of 2.7 mT for 16^{3-} . This difference is visualized in Figure 6 which reproduces the pertinent spectra on the same magnetic field scale.

(50) Gerson, F.; Heckendorn, R.; Möckel, R. *J. Chem. Soc., Chem. Commun.* **1985**, 689.

(51) Gerson, F.; Heckendorn, R.; Möckel, R.; Vögtle, F. *Helv. Chim. Acta* **1985**, *68*, 1923.

(52) Gerson, F.; Heilbronner, E.; Weidmann, B. *Helv. Chim. Acta* **1964**, *47*, 1951.

(53) See, e.g.: Torrance, J. B. *Acc. Chem. Res.* **1979**, *12*, 79.

(54) Rieger, Ph. H.; Bernal, I.; Reinmuth, W. H.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 683.

(55) See footnote 22 of ref 14.

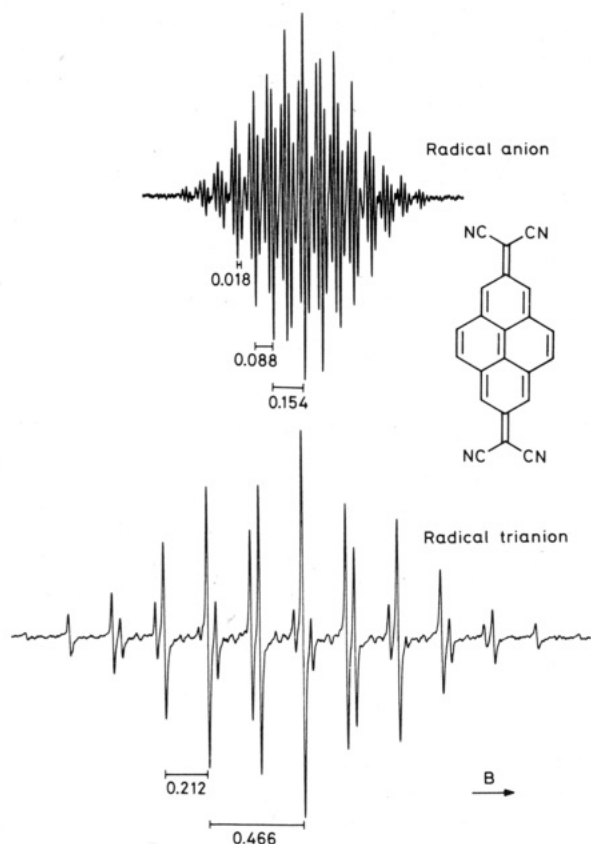


Figure 6. ESR spectra of $16^{\bullet-}$ and $16^{\bullet3-}$: solvent, DME; temperature, 273 K ($16^{\bullet-}$) and 233 K ($16^{\bullet3-}$). All values in mT. From ref 14.

The third half-wave reduction potentials, $E_{1/2}^{(3)}$, which are relevant to the ease of formation of the radical trianions, have been estimated as -3.23 V (vs. SCE) for both 14 and 15 and as -2.60 V for 16.¹⁴ Although a substantially less negative $E_{1/2}^{(3)}$ value of -2.06 V⁵⁶

is indicated by the cyclic voltammogram of the recently synthesized tetracyano-9,10-anthraquinodimethane (17),^{56,57} attempts to observe the ESR spectrum of $17^{\bullet3-}$ have failed because of the low kinetic stability (persistence) of this radical trianion.⁵⁶

Concluding Remarks

The occurrence of π -radical trianions, which can be both detected and characterized by ESR and ENDOR spectroscopy, widens the research area of paramagnetic organic molecules. Despite their high negative charge, it is possible to interpret the structure of these radical trianions by the same simple π -MO models as those used for the radical anions. Since the singly occupied orbitals in the radical anion and in the corresponding radical trianion differ in their nodal properties, the major π -spin populations in the two species reside not only on different atoms but also frequently in different regions of the molecular framework. Due to this dissimilar π -spin distribution, the differences in the physical and chemical behavior of the radical anions and the radical trianions should go beyond those expected on grounds of the unequal charges. One is therefore justified in considering the radical trianions as new molecular species, of which only a relatively small number has hitherto been investigated. The surface of this research area has hardly been scratched, but the list of known radical trianions is steadily growing and will do so in the near future.

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(56) Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, *107*, 556.

(57) Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618.

(58) Rieger, P. H.; Bernal, I.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1961**, *83*, 3918.

Hydrocarbon Radical Cations

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Introduction

In 1980, the hydrocarbon radical ions which were then known were indexed in Landolt Börnstein. The radical anions occupied 149 pages,¹ but the radical cations occupied only 15 pages,² a ratio of 10 to 1.

John Courtneidge was born in London in 1951. He graduated from the University of Bristol, and after a period teaching chemistry in London schools he completed, in 1981, his Ph.D. at University College London (with A. J. Bloodworth). Since then he has worked at UCL with Professor Davies. He is presently developing a career in commercial horticulture.

Alwyn Davies was born in 1926. He obtained his B.Sc. and Ph.D. degrees at University College London with C. K. Ingold; then after a period as Lecturer at Battersea Polytechnic with J. Kenyon, he returned at UCL in 1953. His research has included studies of organic peroxides, of organometallic compounds, and of free radical reactions.

Yet one can argue that, from both theoretical and experimental viewpoints, this is in inverse ratio to their relative importance.

First (Figure 1), the SOMO of the radical cation corresponds with the HOMO of the parent, and the best way of investigating the electron distribution in RH is to examine the ESR spectrum of $RH^{\bullet+}$.

Second, the radical ions, like the electronically excited states, provide a readily accessible and reactive elec-

(1) Börnstein, *Landolt Numerical Data and Fundamental Relationships in Science and Technology*; Springer-Verlag: West Berlin, 1980; Vol. 9d1, pp 708-856.

(2) Börnstein, *Landolt Numerical Data and Fundamental Relationships in Science and Technology*; Springer-Verlag: West Berlin, 1980; Vol. 9d2, pp 6-20.