

Radical Cations and Anions of Benzo[*c*]cinnolines: An Electron Spin Resonance Study

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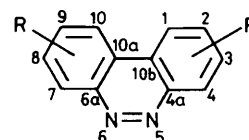
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The radical cations of benzo[*c*]cinnoline and its four symmetrical dimethyl derivatives have been prepared by exposure of the parent compounds as dilute solutions in CFCl_3 to ^{60}Co γ -rays at 77 K. The e.s.r. spectra were all characterised by large hyperfine coupling to two equivalent nitrogen atoms. Analysis of the data gave *ca.* 9% 2s and 44% 2p character on each nitrogen, thereby establishing a σ -structure. Clear deviation from axial symmetry shows that the orbital axes are tilted with respect to each other, an estimate of the angle between the two principle directions being *ca.* 40°. This accords reasonably well with that derived from the p:s ratio of 4.9. The estimated total spin-density on nitrogen is 1.06, showing that the SOMO is strongly localised. Similar treatment of the 2,9- and 3,8-dimethoxy derivatives gave a broad unresolved singlet. This establishes that the SOMO has switched from the σ -(N)-orbital to a π -orbital. Clearly this has very low spin-density on the two nitrogen atoms. We were not able to detect any of the radical cations in the liquid phase. Exposure of dilute solutions of all six compounds as dilute solutions in CD_3OD gave parallel features characteristic of two equivalent ^{14}N nuclei. The perpendicular splittings were close to zero, thus confirming that the SOMO is π , the estimated spin-density on the two nitrogen atoms being *ca.* 34% each. These anions were also prepared in liquid dimethoxyethane and hexamethylphosphoric triamide, and their e.s.r. and ENDOR spectra were recorded. Relative signs of the ^1H coupling constants were obtained using general triple resonance. This has led to full assignments in all cases. Our assignment for the anion of the parent compound differs from that previously proposed.

In various aromatic *N*-heterocycles, such as pyridine, diazines, and cinnolines, the first π -orbital and first lone-pair (*n*)-orbital on nitrogen are close in energy. The order of the π and lone pair ionization potentials is usually determined by photoelectron spectroscopy (p.e.s.) combined with MO calculations. A further source of information, for relaxed radical cations in matrices, is provided by e.s.r. spectroscopy. It has been shown, for example, that pyridine^{1,2} and various diazines^{3,4} generate σ -radical cations on γ -irradiation of dilute solutions in fluorinated solvents at 77 K, in agreement with p.e. predictions. Substitution modifies the ionization energies and can invert the order of the highest filled *n* and π levels. This has been demonstrated in the pyridine series by alkyl substitution,² and recent e.s.r. studies of various *s*-tetrazines clearly traced the switch in wave function from σ to π .^{5,6}

In this paper we present results of a similar study of benzo[*c*]cinnoline (1) and derivatives (2)–(7). In the p.e. spectrum of (1) the shoulder at the low energy side of the first band system, enclosing $n_1 + \pi_1 + \pi_2$, has been assigned to the n_1 level.⁷ In accord with this (1) generates a σ -radical cation on γ -irradiation.³ In the p.e. spectra of (2)–(7), however, this shoulder is completely covered by the low energy band system.⁸ Therefore e.s.r. spectroscopy has been used in order to gain information about any switch in the wave function from σ to π . In particular it was expected that donor substituents in the 2,9 and 3,8 positions should lift π_1 above n_1 . The cations have been prepared by exposing dilute solutions of (1)–(7) in CFCl_3 to ^{60}Co γ -rays at 77 K. This procedure is known to give good yields of the parent cations of many substrates.⁹ All attempts to prepare these cations in liquid phase failed.

It was also of interest to study the corresponding radical anions (2^{-•})–(7^{-•}). The parent anion (1^{-•}) has been



- (1) R = H
- (2) R, R = 1, 10 - $(\text{CH}_3)_2$
- (3) R, R = 2, 9 - $(\text{CH}_3)_2$
- (4) R, R = 3, 8 - $(\text{CH}_3)_2$
- (5) R, R = 4, 7 - $(\text{CH}_3)_2$
- (6) R, R = 2, 9 - $(\text{OCH}_3)_2$
- (7) R, R = 3, 8 - $(\text{OCH}_3)_2$

extensively studied in fluid solution by e.s.r. spectroscopy,^{10–13} but those of (2)–(7) have not been reported. Also we know of no previous study of the solid-state e.s.r. spectra of these radical anions. There is currently some ambiguity in the assignment of the e.s.r. coupling constants in (1^{-•}), based on MO studies,^{11,12} in connection with an e.s.r. study of the corresponding 5,6-dihydrobenzo[*c*]cinnoline radical cations.¹⁴

Results and Discussion

Radical Cations.—Exposure of dilute solutions of (1)–(7) in CFCl_3 at 77 K to ^{60}Co γ -rays generated two types of radical cations. The e.s.r. spectra of (1^{+•})–(5^{+•}) are remarkably similar, showing features of two equivalent ^{14}N nuclei with a maximum separation of *ca.* 62 G and a minimum separation of *ca.* 43.5 G

Table 1. ^{14}N Hyperfine coupling constants (G)^a together with derived orbital populations (%) / 2 for benzo[*c*]cinnoline radical cations in CFCl_3 at 77 K.

	A_x	A_y	A_z	A_{iso}	$2B$	a_s^2	a_p^2
(1 ⁺)	43	62	46	50.3	14.6	9.1	44
(2 ⁺)	42	61	45	49.3	14.6	9.0	44
(3 ⁺)	42	61.5	45	49.5	15	9.0	45
(4 ⁺)	42	61	45	49.3	14.6	9.0	44
(5 ⁺)	42	61	45	49.3	14.6	9.9	44
(6 ⁺) ^b	0	0	0				
(7 ⁺) ^b	0	0	0				

^a 1 G = 10^{-4} T. ^b Only a broad singlet was detected.

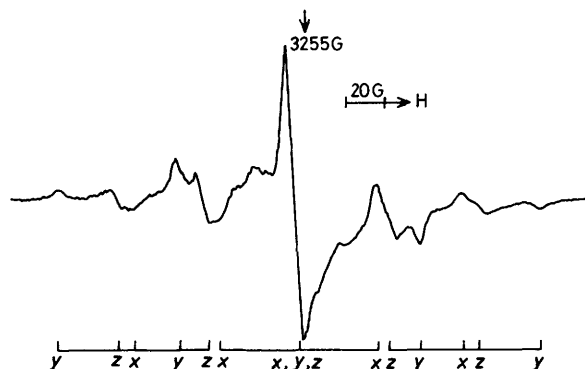


Figure 1. First derivative X-band e.s.r. spectrum for a dilute solution (1:1 000) of 4,7-dimethylbenzo[*c*]cinnoline (5) in CFCl_3 after exposure to ^{60}Co γ -rays at 77 K, showing features assigned to the corresponding radical cation.*

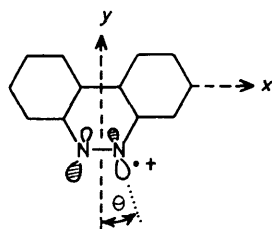


Figure 2.

with a small deviation from axial symmetry. E.s.r. parameters are given in Table 1, and a typical spectrum is shown in Figure 1. Undoubtedly (1⁺)–(5⁺) are $\sigma(n)$ -radical cations with a SOMO of the type shown in Figure 2. Our spectra show only the *x*, *y*, and *z* feature for hyperfine coupling to two equivalent ^{14}N nuclei. Kato and Shida³ quote proton coupling constants as well for four different pairs of protons. However, it is probable that they are based on theoretical 'expectation' rather than on any resolution. Our coupling constants for ^{14}N are close to theirs except that our *x*–*y* splitting is slightly larger than theirs. A non-axial hyperfine tensor is expected for the SOMO shown in Figure 2 provided the axes of the orbitals on nitrogen are not parallel. In that case, A_z , normal to the radical plane is a true perpendicular value, but A_x and A_y seem to be partially averaged, the turning points occurring along the symmetry axes rather than the orbital axes. In that case, using the calculated values of A_{iso} , 'true' A'_x and A'_y values can be obtained, and hence

* Rieger has analysed the line positions of this spectrum, by a least-squares fit, to second order in perturbation theory. The simulation gave best agreement with experiment for A_x 40.5, A_y 62.5, A_z 47.2 G, and $\alpha \pm 5^\circ$ (α is the angle between the *g* tensor *x* and *y* axes and the hyperfine tensor *x* and *y* axes).

Table 2. ^{14}N Hyperfine couplings constants (G)^a together with derived orbital populations (%) / 2 for benzo[*c*]cinnoline radical anions in CD_3OD at 77 K.

	A_{\parallel}	A_{\perp}	A_{iso}	$2B$	a_s^2	a_p^2
(1 ⁻)	17	≈ 0	5.7	11.3	1.0	34
(2 ⁻)	17	≈ 0	5.7	11.3	1.0	34
(3 ⁻)	17.5	≈ 0	5.8	11.7	1.0	35
(4 ⁻)	16.5	≈ 0	5.5	11.0	1.0	33
(5 ⁻)	16	≈ 0	5.3	10.7	1.0	32
(6 ⁻)		≈ 0				
(7 ⁻)	16	≈ 0	5.3	10.7	1.0	32

^a 1 G = 10^{-4} T.

the 2s and 2p orbital populations can be estimated in the usual manner.¹⁵ The results are included in Table 1. In the particular case of the unsubstituted cation (1⁺) we have used the simplified concept that the coupling follows a $(3\cos^2\theta - 1)$ law, we find a value of θ ca. 20° fits the data. This accords with a tendency towards bonding between the two orbitals, and possibly an increase in the ring C–N–N bond angles. It also agrees qualitatively with that estimated from the *p/s* ratio of ca. 4.9. If the simplified assumption or orbital-following is used, this requires a C–N–N bond-angle of ca. 134° . This increase is a limiting value, the real increase is likely to be smaller.

It is curious that for the *s*-tetrazine cations, axial symmetry was found for the ^{14}N hyperfine coupling constants. It is difficult to see why this should be the case in the light of the present results, and in terms of expectation. Possibly the expected deviation from axial symmetry was lost within the rather broad 'perpendicular' features.^{5,6} It seems that methyl substitution has very little effect on the SOMO for these $\sigma(n)$ cations.

Results for the dimethoxy derivatives (6⁺) and (7⁺) were quite different. No ^{14}N hyperfine features were obtained, the spectrum being a simple intense line with *g* ca. 2.002, and a width between points of maximum slope of *g* ca. 12 G. This is clearly due to the π -cation, the SOMO of which must have low density on the two nitrogen atoms. Thus the expected orbital switch occurs between $R^2 = R^9 = \text{CH}_3$ (2⁺) or $R^3 = R^8 = \text{CH}_3$ (3⁺) and $R^2 = R^9 = \text{OCH}_3$ (6⁺) or $R^3 = R^8 = \text{OCH}_3$ (7⁺).

All attempts to prepare these radical cations in the liquid-phase, using methods previously described,^{5,6} were unsuccessful. This is not surprising for the $\sigma(n)$ cations, radicals of this class have never been detected by e.s.r. spectroscopy in the liquid-phase. However, it is perhaps surprising for the π -cation (two OCH_3) since such π -cations are generally more stable.

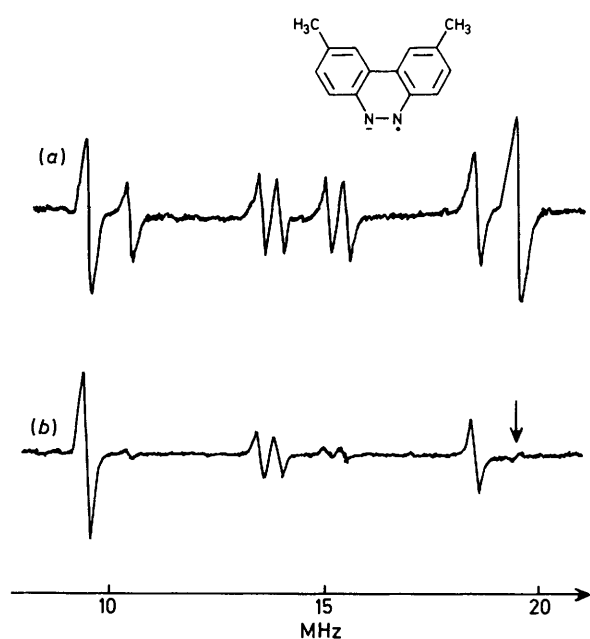
Radical Anions.—These were conveniently generated in the solid-state by exposing dilute solutions of (1)–(7) in CD_3OD at 77 K to ^{60}Co γ -rays. This procedure is known to generate radical anions by electron addition. CD_3OD is preferred over CH_3OH because the e.s.r. signals from solvent radicals are thereby confined to a small central region of the spectrum. All radical anions gave four well defined parallel features flanking the intense solvent line, which are assigned to the $M_i = \pm 2$ and ± 1 lines. These gave $A_{\parallel} (^{14}\text{N})$ ca. 17 G for two equivalent ^{14}N nuclei. The perpendicular (^{14}N) coupling was too small to be resolved, in marked contrast with our results for the $\sigma(n)$ cations (Table 2). Using the isotropic data listed in Table 3, we calculate that A_{\perp} must be ca. -1 G, which explains our inability to detect these features. This is a common finding for π -radicals, and it shows conclusively that these species are indeed the expected π^* -anions. The estimated 2p character is ca. 34% giving a total spin density of ca. 68% on nitrogen.

E.s.r. and ENDOR spectra of (1⁻) in the liquid phase have

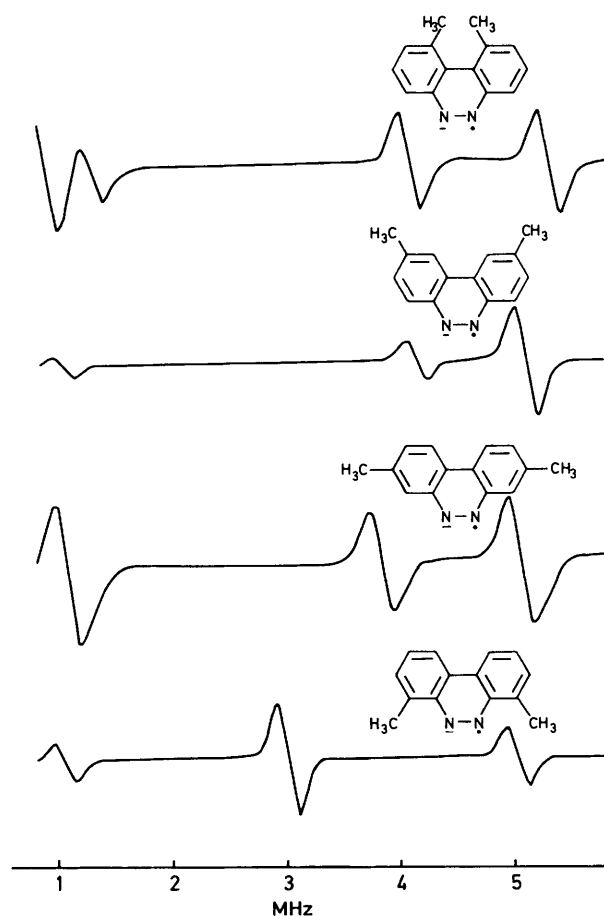
Table 3. Isotropic hyperfine coupling constants for the benzo[*c*]cinnoline radical anions (1⁻)–(7⁻) in HMPT at 300 K (e.s.r.) or in DME at 230 K (ENDOR), together with literature data for (1⁻).

	Method	$a(\text{N})/\text{G}$	$a(\text{H}^{1-10})/\text{G}$	$a(\text{H}^{2,9})/\text{G}$	$a(\text{H}^{3,8})/\text{G}$	$a(\text{H}^{4,7})/\text{G}$	g
(1 ⁻)	E.s.r. ^a	5.27	0.77	2.83	0.28	3.58	
	E.s.r. ^b	5.20	0.78	2.86	0.26	3.64	
	ENDOR ^c		0.76	2.86	0.34	3.52	
	E.s.r. ^d	4.94	0.81	2.91	0.17	3.66	
	ENDOR		+0.29	-3.58	+0.76	-2.86	
(2 ⁻)	E.s.r.	5.27	0.50 ^e	3.83	0.85	2.86	2.0032
	ENDOR		-0.60 ^e	-3.73	+0.87	-2.86	
(3 ⁻)	E.s.r.	5.30	0.33	3.70 ^e	0.73	2.97	2.0034
	ENDOR		+0.41	+3.60 ^e	+0.71	-2.91	
(4 ⁻)	E.s.r.	5.10		3.62	0.75 ^e	2.85	2.0034
	ENDOR		+0.26	-3.60	-0.75 ^e	-2.73	
(5 ⁻)	E.s.r.	4.80	0.33	3.62	0.76	2.15 ^e	2.0034
	ENDOR		+0.36	-3.55	+0.75	+2.09 ^e	
(6 ⁻)	E.s.r.	5.55				3.10	2.0035
	ENDOR		+0.26		+0.53	-3.07	
(7 ⁻)	E.s.r.	5.00		3.82		2.55	2.0034
	ENDOR		+0.20	-3.76		-2.52	

^a Electrochemical reduction in dimethylformamide (DMF) at 300 K.¹¹ ^b Reduction with Na in DMF at 300 K.¹³ ^c Reduction with Na in DME at 191 K.¹³ ^d Reduction with Na in HMPT at 293 K.¹² ^e 6H (CH₃).

**Figure 3.** ¹H ENDOR spectrum of (3⁻) in DME at 230 K (a) together with the general triple resonance spectrum, pump frequency 19.50 MHz (b).

been studied in detail¹⁰⁻¹³ and have given all the ¹H and ¹⁴N coupling constants (see Table 3) which were assigned on the basis of MO calculations.^{11,12} We generated (1⁻)–(7⁻) in dimethoxyethane (DME) or in hexamethylphosphoric triamide (HMPT) by reduction of the corresponding benzo[*c*]cinnolines with potassium metal. In the ENDOR spectra [see, for example, Figure 3(a)] all ¹H coupling constants were clearly detected and, in addition, by performing general triple resonance experiments¹⁶ [Figure 3(b)] relative signs were determined. Figure 4 shows special triple resonance spectra¹⁶ of (2⁻)–(5⁻), in which signal intensities qualitatively reflect multiplicities of different sets of equivalent protons. So the 1:3 intensity ratios can be easily seen. The resulting data are given in Table 3. The analysis of the e.s.r. spectra in DME is hampered

**Figure 4.** ¹H Special triple resonance of (2⁻)–(5⁻) in DME at 230 K.

because of the additional splittings of the counter-ion, K⁺. Therefore we also measured e.s.r. spectra of (1⁻)–(7⁻) in HMPT where the counter-ion is solvated and gives no hyperfine contribution. In most examples the e.s.r. spectra are well resolved and are well simulated with the values given in Table 3. The isotropic nitrogen splitting is *ca.* 5 G in all cases. Methyl

substitution replaces the α -proton coupling constant by a methyl proton splitting very close in magnitude, but of opposite sign. Using this relation the e.s.r. results of (2⁻)-(5⁻) yield a complete, unambiguous, assignment of all ¹H coupling constants in (1⁻). As in the related 5,6-dihydrobenzo[*c*]-cinnoline radical cation¹⁴ the larger of the negative proton splittings, $a(\text{H}) - 3.58$ G, is assigned to the protons in positions 2 and 9, the smaller, $a(\text{H}) - 2.86$ G, to 4- and 7-H. For the positive proton coupling constants, the assignment $a(\text{H}^{3,8}) + 0.76$ and $a(\text{H}^{1,10}) + 0.29$ G is obtained. This experimental assignment differs from that reported in the literature, based on MO studies.¹¹⁻¹³ These calculations proposed negative signs for all proton splittings in (1⁻) and suggested the following assignment: $a(\text{H}^{4,7}) - 3.64$, $a(\text{H}^{2,9}) - 0.286$, $a(\text{H}^{1,10}) - 0.78$, and $a(\text{H}^{3,8}) - 0.26$ G.^{11,12}

Neglecting the hidden spin-densities in the positions 4a, 6a, 10a, and 10b, the proton splittings of (1⁻) [$a(\text{H}) = -27\rho_{\text{C}}^{\pi}$] indicates a total spin-density of $[2(-3.58 - 2.86 + 0.76 + 0.29)/-27]$ *ca.* 0.40 for the diphenyl component. This value can increase to *ca.* 0.5 depending on the relative magnitudes of $+\rho_{\text{C}10\text{a}}^{\pi}$ and $(-)\rho_{\text{C}4\text{a}}^{\pi}$. Together with the spin density on both nitrogens, *ca.* 0.68, one obtains a total of *ca.* 1.08-1.18. The deviation from unity is connected with the margin of error of the relationships applied, and probably to the presence of some negative densities.

Experimental

¹H N.m.r. spectra were obtained with a Bruker AM 500 instrument for [²H₆]dimethyl sulphoxide solutions at room temperature, with tetramethylsilane as an internal standard. Mass spectra were taken on a Dupont 21-492 instrument.

Benzo[*c*]cinnoline (1), obtained commercially, was purified by recrystallisation from benzene. Derivatives (2),¹⁷ (3),¹⁸ (4),¹⁹ (5),²⁰ (6),²¹ and (7)²¹ were prepared following the literature procedures. As to the last step of their synthesis it was generally of advantage to cyclize the substituted 2,2'-dinitrodiphenyl compounds using the lithium aluminium hydride reduction method of Corbett and his co-workers;²² an example is given below.

1,10-Dimethylbenzo[*c*]cinnoline (2).—This had m.p. 112-113 °C (lit.,¹⁷ 113-114 °C); δ 2.59 (6 H, s, CH₃), 7.86 (2 H, d, *J* 7.2 Hz, 2-, 9-H), 7.94 (2 H, dd, *J* 7.9, 7.2 Hz, 3-, 8-H), and 8.50 (2 H, d, *J* 7.9 Hz, 4-, 7-H); *m/z* 208 (*M*⁺, 100%).

2,9-Dimethylbenzo[*c*]cinnoline (3).—This had m.p. 187 °C (lit.,¹⁸ 188 °C); δ 2.66 (6 H, s, CH₃), 7.82 (2 H, d, *J ca.* 7 Hz, 3-, 8-H), 8.53 (2 H, d, *J ca.* 8 Hz, 4-, 7-H), and 8.64 (2 H, s, 1-, 10-H); *m/z* 208 (*M*⁺, 100%).

3,8-Dimethylbenzo[*c*]cinnoline (4).—This had m.p. 187 °C (lit.,¹⁹ 188 °C); δ 2.64 (6 H, s, CH₃), 7.84 (2 H, dd, *J* 8.3, 1.6 Hz, 2-, 9-H), 8.43 (2 H, d, *J* 1.5 Hz, 4-, 7-H), and 8.71 (2 H, d, *J* 8.3 Hz, 1-, 10-H); *m/z* 208 (*M*⁺, 100%).

4,7-Dimethylbenzo[*c*]cinnoline (5).—This had m.p. 167-168 °C (lit.,²⁰ 169-170 °C); δ 3.09 (6 H, s, CH₃), 7.83 (2 H, d, *J* 7.2 Hz, 3-, 8-H), 7.92 (2 H, dd, *J* 8.2, 7.2 Hz, 2-, 9-H), and 8.77 (2 H, d, *J* 8.2 Hz, 1-, 10-H); *m/z* 208 (*M*⁺, 100%).

2,9-Dimethoxybenzo[*c*]cinnoline (6).—To a stirred suspension of 5,5'-dimethoxy-2,2'-dinitrobiphenyl (3.04 g, 10 mmol) in diethyl ether (300 cm³) and benzene (300 cm³) lithium aluminium hydride (2.28 g, 60 mmol) was added. Then the mixture was stirred under reflux for 2 h. After cooling to room temperature the excess of hydride was decomposed with water (*ca.* 5 cm³). The filtrate of the mixture was evaporated under reduced pressure. Chromatography of the residue on

Merck silica gel using methylene chloride-ethyl acetate as eluant gave (6) (840 mg, 35%) as crystals from methanol, m.p. 169-170 °C (lit.,²¹ 166-169 °C); δ 4.09 (6 H, s, OCH₃), 7.57 (2 H, dd, *J* 9.1, 2.6 Hz, 3-, 8-H), 8.18 (2 H, d, *J* 2.6 Hz, 1-, 10-H), and 8.50 (2 H, d, *J* 9.1 Hz, 4-, 7-H); *m/z* 240 (*M*⁺, 100%).

3,8-Dimethoxybenzo[*c*]cinnoline (7).—This had m.p. 200-201 °C (lit.,²¹ 197 °C); δ 4.04 (6 H, s, OCH₃), 7.63 (2 H, dd, *J* 9.0, 2.6 Hz, 2-, 9-H), 8.05 (2 H, d, *J* 2.7 Hz, 4-, 7-H), and 8.72 (2 H, d, *J* 9.1 Hz, 1-, 10-H); *m/z* 240 (*M*⁺, 100%).

Samples were γ -irradiated at 77 K in a Vickrad ⁶⁰Co γ -ray source at a dose rate of *ca.* 0.8 Mrad h⁻¹ for up to 1 h. E.s.r. spectra were recorded directly after exposure at 77 K on a Varian E 109 spectrometer. Samples were annealed to the m.p. of the solvents (CFCl₃, CD₃OD), but showed no significant secondary products prior to loss of signal. E.s.r., ENDOR, and triple resonance spectra of the radical anions in liquid-phase were measured with a Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system; *g* values were determined by using an n.m.r. gaussmeter and the Hewlett-Packard frequency converter 5246 L. This was calibrated with the perylene radical cation.

Acknowledgements

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