Pergamon

Tetrahedron Vol. 51, No. 27, pp. 7451-7458, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/95 $9.50+0.00

0040-4020(95)00371-1

Chemical and Electrochemical Reduction of the Products from the Reactions of Isoindolines and Tetracyanoethylene

Patricia Carloni, Lucedio Greci,* Pierluigi Stipa

Dipartimento di Scienze dei Materiali e della Terra, Università, I-60131 ANCONA, Italy

Dietrich Döpp, Alaa El-Din Abdel Hafeez Hassan

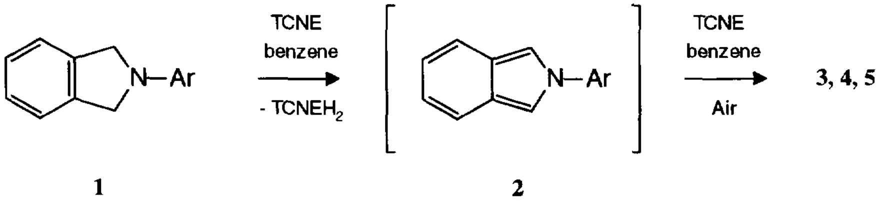
Fachgebiet Organische Chemie, Universität, D-4100 DUISBURG, Germany

Angelo Alberti

I.Co.C.E.A. - CNR, Area della Ricerca, I-40129 BOLOGNA, Italy

Abstract: The reduction potentials of compounds resulting from the title reaction and containing one (**4**) or two (**3**) dicyanovinylidene moieties have been determined by means of cyclic voltammetry. Electrochemical reduction of the same compounds within the cavity of an EPR spectrometer led to the observation of radical species tentatively identified as the corresponding radical anions. EPR experiments have also provided indication that the first formed species in the butoxide reduction of **3** undergoes cleavage of the bond between the two heterocyclic systems evolving to radical anions identical to those obtained by similar reduction of compounds **4**. Some models compounds have also been investigated for comparison purposes.

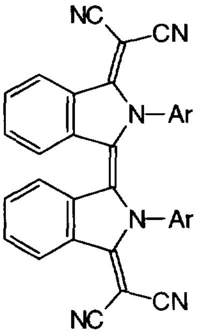
Tetracyanoethylene as well as its derivatives containing the dicyanovinylidene moiety are electron-deficient substances, and it is well known that their monoelectronic reduction usually results in the formation of fairly long-lived radical anions;[1] this also applies to other species containing cyano groups bound to a double bond, such as N,N'-dicyanoquinone diimines.[2] Tetracyanoethylene is also known to readily form stable charge-transfer complexes when reacted with suitable electron-rich derivatives, such as hexamethylbenzene or thionaphthoindole,[3,4] or with metallocenes.[5,6] The electron-transfer salts formed in the latter case may be considered examples of organic magnets.[7]



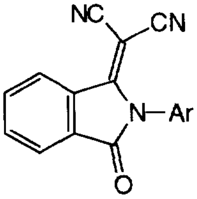
a: Ar = C_6H_5; **b**: Ar = C_6H_4-OCH_3(p); **c**: Ar = C_6H_4-OCH_3(m); **d**: Ar = C_6H_4-CH_3(p); **e**: Ar = C_6H_4-CH_3(m)

Scheme 1

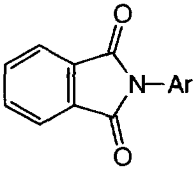
On the other hand the reaction of tetracyanoethylene with isoindolines **1a-e** has been found to proceed through the formation of labile charge-transfer complexes; these, most likely via dehydrogenation of the isoindolines **1** to isoindoles **2**, under aerated conditions, evolve to compounds **3a-e-5a-e**,[8] which still exhibit significant electron-accepting properties (Scheme 1).



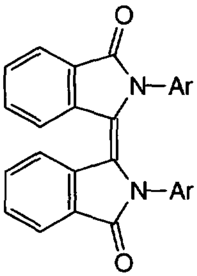
3a-d



4b,c



5b,c



6b

In the present paper we report on the EPR studies of the radical anions obtained by chemical and electrochemical reduction of compounds **3a-d**, **4b,c** and **5b,c** and on the cyclic voltammetry performed on compounds **3c** and **4c**. Moreover compound **6b** has been included in this study for comparison.

Compounds **3** and **6** might exist as E/Z geometrical isomers. Indeed in a previous paper[9] concerning the reaction of N-aryl isoindoline with 2,3-dicyanonaphthoquinone the formation of two geometrical isomers of **6b** has been suggested, neither of which has however been characterised or associated with a particular set of spectral data. Coming to our case, the X-ray structure of **3e** indicated a Z conformation with a 37° dihedral angle between the planes of the two isoindoline moieties.[8] The similarity of the ^{1}H-NMR parameters measured for **3a-d** e **6b** with those of **3e** suggests that the compounds dealt with the present paper can be safely assigned a similar Z geometry. Actually, the very suggestion of the existence of an E/Z geometrical isomerism for compound **6** appears to be questionable on the basis of the spectral data given in the same reference.[9] Indeed if the E geometry were existent, one would have to postulate that the 4 and 4' H atoms (by assuming the dimeric linkage between positions 3 and 3') would deeply penetrate the electron clouds of the N-phenyl rings, with a consequent enormous diamagnetic shielding, which in fact is not observed. Inspection of molecular models indicates that the E isomers are highly biased, whereas the Z isomers can nicely relieve the hindrance by simple twisting.

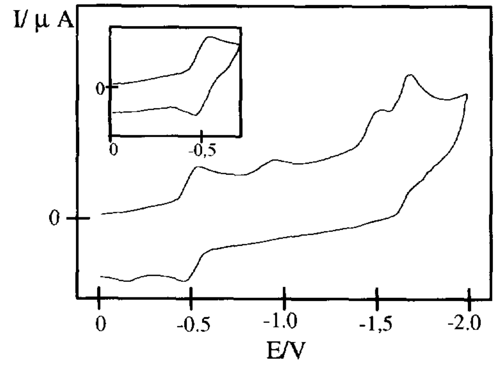


Fig. 1. Cyclic voltammogram of compound **3c** in DMF/TEAP. The inset shows the full reversibility of the first reduction wave.

RESULTS

Cyclic Voltammetry

As preliminary experiments indicated that the presence, nature and position of a substituent in the *N*-aryl ring were irrelevant to the electrochemical parameters of the compounds, a full investigation was performed using compounds **3c** and **4c** as representative substrates, and the dicarbonyl derivative **6b**. The observed peak potentials are collected in Table 1.The cyclic voltammogram of **3c** in DMF/Et_4NClO_4 (TEAP) over a wide potential span (0 ÷ 2.0 V) exhibits three cathodic peaks at E'_{pc} = - 0.54, - 0.94 and - 1.54 V *vs.*

SCE (see Figure 1 and Table 1). When the voltammetry is carried out with a potential span limited to the first polarographic wave, a well defined cathodic-anodic system is obtained. The first reduction wave is associated with the formation of the radical anion of the starting compound, **3c**$^{\bullet -}$, and its full reversibility, as deduced by the fact that it shows $i_{pa}/i_{pc} \cong 1$ and $E'_{pa} - E'_{pc} = 70\text{-}80$ mV at all scan rates used ($0.05 \div 2.00$ V s^{-1}), indicates that this species is stable under the experimental conditions.

Table 1. Reduction-Peak Potentials, E_{pc}, for Compounds **3c**, **4c**, **5a** and **6b** in DMF/TEAP *vs.* SCE.

Compound	E'_{pc}/V	E''_{pc}/V	E'''_{pc}/V	Reference
3c	-0.54	-0.94	-1.54	This work
4c	-0.92	-1.43	-	This work
5a	-1.37	-	-	10
6b	-1.25	-1.55	-	This work

It seems conceivable to associate the second reduction wave with the formation of a dianion, this species being however unstable as indicated by the small height of the peak and by the absence of an appropriate anodic counterpart in the cyclic voltammetry. Although it is known that molecules containing the dicyanovinylidene moiety may accommodate three extra electrons to give radical trianions,[1f] the third reduction wave cannot in this case be safely assigned to such a species. It is indeed more likely that this wave originates from the reduction of an adventitious species of some sort resulting from the evolution of the unstable dianion.

The reduction of compound **4c** containing only one dicyanovinylidene moiety leads to the observation of two well defined reduction waves (see Table 1); only the first reduction step, occurring at - 0.9 V *vs.* SCE, is fully reversible and it is attributed to the formation of the persistent radical anion **4c**$^{\bullet -}$, while the wave observed at more negative potentials, and attributed to the formation of the dianion **4c**$^{2-}$, does not show any significant anodic counterpart.

A similar behaviour was exhibited by compound **6b** whose reduction leads to the observation of a reversible wave at - 1.25 V (see Table 1) associated to the formation of the radical anion **6b**$^{\bullet -}$, and to an irreversible second wave attributed to the formation of the dianion **6b**$^{2-}$.

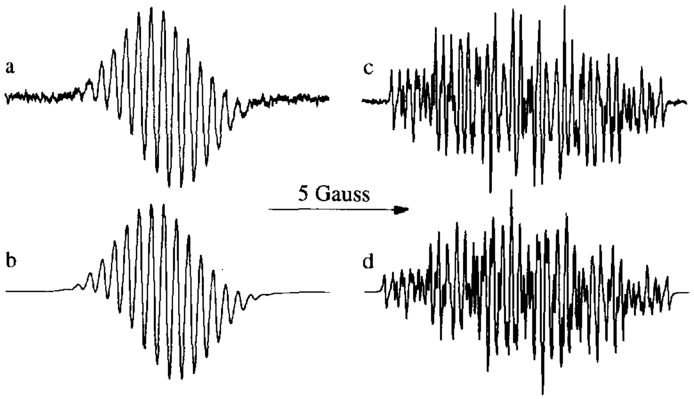


Fig. 2. Initial (a) and final (c) experimental spectra obtained in the *tert*-butoxide reduction of **3b** in DMSO, together with the corresponding computer simulations (b) and (d).

EPR studies

The reduction of compounds **3**-**6** under different conditions allowed the EPR detection of several radical species whose hyperfine spectral parameters are collected in Table 2.

Upon electrochemical reduction of a DMF/Et_4NClO_4 solution of **3c** inside the cavity of an EPR spectrometer, a 17 equally spaced line spectrum was recorded; the signal appeared at potentials close to - 1.0 V, and no other species were detected by increasing the applied potential to - 2.5 V, the only observed effect being a faster decrease of the intensity of the signal.

Table 2. EPR spectral parameters for the radicals observed upon chemical or electrochemical reduction of compounds **3a-d**, **4b,c**, **5b,c**, and **6b**.[a]

Compound	Radical	hfsc/G	*g*	Reducing agent
3c	**3c**$^{\bullet -\,b}$	0.45(4N), 1.00(2N)	2.0024$_5$	Electrochemical/DMF
3a-d	**3a-d**$^{\bullet -\,b,\,c}$	0.47(4N), 0.97(2N)	2.0024$_5$	^{t}BuOK/DMSO
3a-d	**4a-d**$^{\bullet -\,d}$	0.37(1N), 0.52(1H), 0.85(1N), 1.15(1H), 1.48(1H), 2.02(1H), 2.40(1N)	2.0031$_5$	^{t}BuOK/DMSO
4b,c	**4b,c**$^{\bullet -}$	0.37(1N), 0.52(1H), 0.85(1N), 1.15(1H), 1.48(1H), 2.02(1H), 2.40(1N)	2.0031$_4$	Electrochemical/DMSO
5b,c	**5b,c**$^{\bullet -}$	0.28(2H), 2.34(2H), 2.47(1N)	2.0038$_3$	Bu$_4$NBH$_4$/^{t}BuOH/hv
6b	**6b**$^{\bullet -}$	0.43(4H), 0.86(2H), 0.96(2H9, 1.29(2N)	2.0032$_8$	Bu$_4$NBH$_4$/^{t}BuOH/hv

[a]) Compounds with different substituents on the N-phenyl ring gave identical spectra; [b]) Tentative identification; [c]) Initial spectrum;[d]) Final spectrum

An almost identical spectrum was observed by reduction of compound **3b** with potassium *tert*-butoxide in a deoxygenated DMSO solution (Figure 2a); actually, reduction of compounds **3a-d** led to the observation of completely superimposable spectra, regardless of the presence and the nature of the substituent on the *N*-phenyl ring. The signal had a *g*-factor of 2.0024$_5$, and the simulation shown in Figure 2b could be obtained by assuming coupling of the unpaired electron with a set of 4 equivalent nitrogen atoms and a second set of 2 equivalent nitrogen atoms.

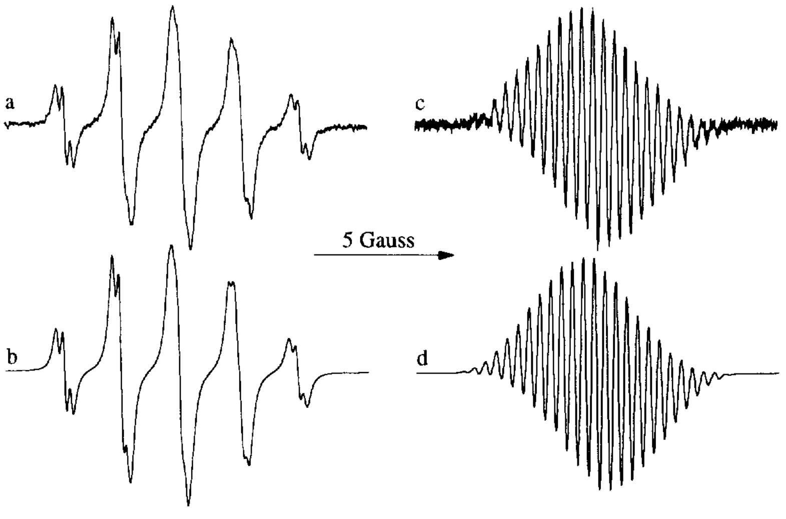


Fig. 3. Experimental (a and c) and computer simulated spectra (b and d) of the radical anions **5b**$^{\bullet -}$ and **6b**$^{\bullet -}$ obtained in the Bu$_4$NBH$_4$/^{t}BuOO^{t}Bu photoinduced reduction of **5b** and **6b** in benzene.

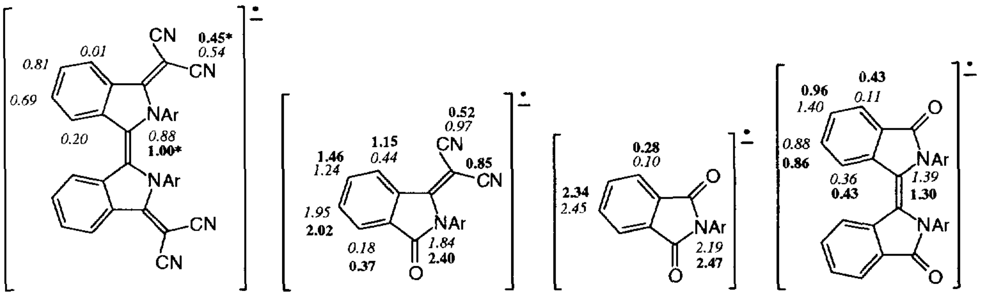
In all cases the spectrum observed in the butoxide reduction of **3** evolved with time and eventually the original signal was completely replaced by the one shown in Figure 2c which persisted for several hours without further noticeable variations. The time required for the appearance of this second spectrum varied drastically with the amount of potassium *tert*-butoxide used for the reduction: thus with small amounts of reducing agent the initial spectrum persisted for a few hours, while with higher ^{t}BuO$^-$ concentrations the evolution was faster, and in some cases the modified spectrum was the first and only observed signal. This last spectrum had a *g*-factor of 2.0031$_5$ and indicated the interaction of the unpaired electron with three non equivalent nitrogen and four non equivalent hydrogen nuclei (see simulation in Figure 2d and parameters in Table 2).

The reduction of compounds **5b-c** and **6b** with potassium *tert*-butoxide in DMSO did not lead to the detection of any EPR signal; spectra could instead be recorded when treating these derivatives with Bu_4NBH_4/^{t}BuOO^{t}Bu in ^{t}BuOH under UV irradiation, a convenient method for the generation of the radical anions of several species.[11] The EPR spectrum observed for the radical anion $\mathbf{5}^{\bullet -}$ (see Figure 3a for $\mathbf{5b}^{\bullet -}$) originated from the interaction of the unpaired electron with two sets of two equivalent protons and a nitrogen atom with couplings (Table 2) in agreement with those reported in the literature for the radical anion of phthalimide.[12] The similar reduction of **6b** lead to the more complex spectrum of $\mathbf{6b}^{\bullet -}$ (Figure 3c) which although containing a greater number of lines had a pattern similar to that initially observed for $\mathbf{3c}^{\bullet -}$. Consistent with the structure of the starting compound, the spectrum was simulated (see Figure 3d) by assuming coupling of the unpaired electron with four equivalent protons, two sets of two equivalent protons and two equivalent nitrogen atoms with the hyperfine parameters given in Table 2.

Surprisingly, the reduction of **4** with either potassium *tert*-butoxide or tetrabutylammonium borohydride failed to lead to the detection of the corresponding $\mathbf{4}^{\bullet -}$. The radical anion could instead be generated by electrochemical reduction of the parent compound in a DMSO/TEAP solution and its EPR spectrum proved identical to the final one observed in the butoxide reduction of compound **3**.

DISCUSSION

The first reduction wave of the examined compounds is attributed to the formation of the corresponding radical anions which must be rather persistent species as indicated by the full reversibility of the cyclic voltammograms. The trend of the peak reduction potentials given in Table 1 reflects expectations, indicating the greater electron-withdrawing ability of the dicyanovinylidene group as compared to that of the carbonyl function. Thus, the most easily reducible compounds are the tetracyano derivatives **3**, followed by compounds **4**, containing one dicyanovinylidene moiety and a carbonyl group, while reduction of the dicarbonyl derivatives **5** and **6** takes place at more negative potentials, in line with their more pronounced amidic nature.



3 **4** **5** **6**

Fig. 4. Experimental (bold) and calculated (italic) hfsc for the radical anions from compounds **3-6**. The asterisk denotes tentative assignments.

The hyperfine parameters derived from the EPR spectra observed in the electrochemical reduction as well as from those initially observed by the butoxide reduction of compounds **3** are slightly puzzling and deserve some comments. Indeed, the potential at which the signals are observed (ca. -1.0 V) suggests that they could be due to the radical anions $3^{\bullet -}$; on the other hand, the value of their *g*-factor is somewhat lower than expected for such species and doubts on the actual identity of the radicals also originate from the fact that the hyperfine parameters obtained from the simulations (see Table 2) seem to exclude participation of the protons of the two isoindolinic moieties in the delocalization of the extra electron, this being at odd with the results of McLachlan spin density calculations shown in Figure 4 which on the other hand provide rather good predictions for the splittings of the nitrogen nuclei.

The possibility that the observed spectra are actually due to the radical trianions of compounds **3** can be safely ruled out on the basis of the fact that the potential whose signals appear, i.e. *ca.* -1.0 V, is significantly lower than the one reasonably required for the formation of these species, and that cyclic voltammetry indicates a very low stability of the dianion through which the trianion should form. Further support in this direction is provided by McLachlan spin density calculations that predict for the ring protons of the trianion hfs constants much larger than those experimentally observed.

It should also be emphasized that the coupling constants given in Table 2 should be considered with some caution: actually, because of the particular pattern of the spectrum shown in Figure 2a, the set of parameters obtained in the simulation may not necessarily be the only one correctly reproducing the observed signal.

The attribution of the spectra observed by reduction of compounds **5** and **6** to the corresponding radical anions $5^{\bullet -}$ and $6^{\bullet -}$ was instead straightforward, as the spectra could be interpreted in terms of the interaction of the extra electron with the expected number of hydrogen and nitrogen nuclei, and the good agreement between experimental and calculated couplings clearly emerges from the data in Figure 4.

The failure in producing the radical anions from compounds **4** by chemical reduction is disconcerting as the cyclic voltammetry indicates that their reduction potentials fall well within the interval accessible to the *tert*-butoxide anion as well as to the borohydride;[13] in addition, the reversibility of the first reduction wave of **4** suggests that the radical anions $4^{\bullet -}$ should be rather persistent. Although it is possible that the chemical reduction of **4** results in the formation of diamagnetic dianionic species which would not be detectable by EPR spectroscopy, it seems unlikely that this should only happen with these derivatives, and not with compounds **3** which are characterised by less negative values of the second reduction potential.

The radical anions $4^{\bullet -}$ could instead be generated by electrochemical reduction of **4** in DMSO/TEAP; the parameters obtained from the simulation of their EPR spectra (see Table 2) leave little doubt about the nature of the species under observation, being consistent with the structure of the starting compounds (nature and number of coupled nuclei) and showing good agreement with McLachlan predictions. It may be worth pointing out that the correct simulation of the spectra of $4^{\bullet -}$ indicates the magnetic difference between the nitrogen atoms of the two cyano groups, whereas for radicals $3^{\bullet -}$ the simulations were obtained by assuming an equal coupling for the four CN nitrogen atoms. As already pointed out, however, the hyperfine constants derived from the simulation of the latter species must be considered with caution, in particular it should be borne in mind that the difference in the splittings of the cyano nitrogen atoms may well be smaller than the spectral linewidth, thus leading to their apparent equivalence. The spectra were identical to those resulting from evolution of the signals initially observed in the ^{t}BuOK reduction of compounds **3** (Figure 2c), and on this basis also these latter spectra were assigned to the radical anions $4^{\bullet -}$. The formation of **4** in the reduction of **3** with potassium *tert*-butoxide in DMSO has already been established by Hassan[8] in a *semi*-micro experiment carried out in the presence of a *gentle* stream of dry oxygen. It is quite difficult to propose a reliable mechanism for the formation of $4^{\bullet -}$ under the present experimental conditions (dry, deoxygenated solvent). Although one might envisage that this species is formed *in situ* either by action of the *tert*-butoxide anion or by alcoholysis of **3** brought about by ^{t}BuOH,[#] we do not have any really definite mean to prove the *complete exclusion* of adventitious oxygen from the system. On the other hand, it is not to be excluded that species resulting from polyelectronic reduction of **3**, such as 3^{2-} and $3^{\bullet 3-}$, play an important role in the formation of $4^{\bullet -}$.

[#] In this respect it may be worthwhile recalling that the reduction in the ^{t}BuOK/DMSO system is thought to proceed through proton abstraction from the solvent by the *tert*-butoxide anion (formation of ^{t}BuOH) followed by electron transfer from the resulting $CH_3S(O)CH_2^-$ anion to the electron deficient substrate.[14]

The detection of $\mathbf{4}^{\bullet -}$ upon ^{t}BuOK/DMSO reduction of **3** is somehow reminiscent of what we recently observed with 2-phenyl-3-arylimino-3*H*-indoles, whose reduction under similar conditions initially leads to the formation of the radical anions, which are soon replaced by the radical anions of the corresponding 2-phenyl-3*H*-indole-3-one.

Whatever the mechanism, the failure of detecting the radical anions $\mathbf{4}^{\bullet -}$ by chemical reduction of **4** suggests that in the butoxide reduction of **3** the radical anion $\mathbf{4}^{\bullet -}$ must be formed directly rather than occurring through the initial formation of **4** and its subsequent reduction.

EXPERIMENTAL

Chemicals

Compounds **3a-d**,[8] **4b,c**,[8] **5b,c**[8] and **6b**[9] were available from previous investigations. 2-[1-(3'-Dicyanomethylene-2',3'-dihydro-1'*H*-isoindol-1-yliden)-2,3-dihydro-1*H*-isoindol-3-yliden]propanedinitriles **3a-d** had all been crystallized from acetonitrile. 2,2'-Diphenyl- (**3a**), no melt < 330°; 2,2'-di-(4-methoxyphenyl)- (**3b**), m.p. 325°C; 2,2'-di-(3-methoxyphenyl)- (**3c**), m.p. 270°C; 2,2'-di-(4-methylphenyl)- (**3d**). 3-Dicyanomethylene-2,3-dihydro-1*H*-isoindol-1-ones (**4b,c**); 2-(4-methoxyphenyl)- (**4b**), m.p. 239-241°C (from ethanol); 2-(3-methoxyphenyl)- (**4c**), m.p. 224-226°C (from ethanol). N-(4-Methoxyphenyl)phthalimide (**5b**), m.p. 168°C (ref.[15] 164°C) and N-(3-methoxyphenyl)phthalimide (**5c**), m.p. 124-25°C (ref.[15] 126°C) were both isolated from the reaction mixture and prepared independently. 2,2'-Di-(4-methoxyphenyl)-2,2',3,3'-tetrahydro-bi(1*H*)-isoindolyliden-3,3'-dione (**6b**) had m.p. 292-294°C (from acetonitrile). All other chemicals were purchased from Aldrich and used as received, with the exceptions of DMF (anhydrous 99 %, Aldrich) which was purified according to a previously described protocol[16] and Et_4NClO_4 (TEAP) that was recrystallized from water and dried *in vacuum* at 60°C for three days.

EPR Spectroscopy

EPR spectra were recorded on a Varian E4 and a Bruker ER 200 D spectrometer equipped with a gaussmeter for field calibration and a frequency counter for the determination of the *g*-factors that were corrected with respect to that of the perylene radical cation in concentrated sulphuric acid. The radical anions were obtained either by adding variable amount of potassium *tert*-butoxide to deoxygenated DMSO solutions of the appropriate substrate contained in a flat cell or in a capillary tube or by photolysis of a deoxygenated benzene solution of the compound to be reduced containing some tetrabutylammonium borohydride and di-*tert*-butylperoxide. For electrochemical experiments a small platinum gauze was inserted in a commercial EPR flat cell, the reference and auxiliary electrodes, separated by sintered glass disks, being those used in the voltammetric experiments; in these cases the radical anions were generated at constant potential by electrolysis of carefully deoxygenated DMF or DMSO solutions of products **3c** and **4b,c** (1.5×10^{-3} mol dm^{-3}) and TEAP (0.1 mol dm^{-3}). The electrochemical generation of the radicals was carried out using a potentiostat-intentiostat AMEL 552 coupled with an integrator AMEL 731.

Cyclic Voltammetry

The electrochemical studies were carried out at room temperature in a three electrode cell using nitrogen purged DMF solutions of **3c**, **4c** or **6b** (10^{-3} mol dm^{-3}), containing 0.1 mol dm^{-3} TEAP.

A stationary platinum disk (AMEL 492) of about 1 mm diameter was used as working electrode and a platinum wire as the auxiliary electrode. Hg-Hg_2Cl_2, NaCl (sat.aq.)-DMF-TEAP/sintered glass disk[16] was used as reference electrode. Details of the apparatus and the cell have been described elsewhere.[17] The experiments were performed using a multipolarograph AMEL 472/WR coupled with a digital x/y recorder AMEL 863.

MO calculations

Spin densities calculations were carried out with the McLachlan method on the model compounds shown in Figure 4 using the following parameters for the carbonyl ($h_O = 1.5$, $k_{CO} = 1.6$, $h_{CC'} = 0.9$)[18] and cyano ($h_N =$

1.0, $k_{CN} = 2.0$, $k_{CC'} = 0.9$)[18] substituents and for the heterocyclic nitrogen atom ($h_N = 1.2$, $k_{CN} = 1.0$).[9] For the aromatic ring protons a $Q_{CH} = -23.7$ was employed in the Mc Connel equation, while more complex relations were used to evaluate the nitrogen splitting of the cyano group ($a_N = 23.1\rho_N - 6.8\rho_C$)[1f] and of the heterocyclic nitrogen [$a_N = 30\rho_N + 8(\rho_C+\rho_{C'})$].[9]

ACKNOWLEDGEMENTS

This work was supported by MURST (Rome), Italy.

REFERENCES

1. a: Iieger, P. H.; Bernal, I.; Reinmuth, W. H.; Fraenkel, G. K. *J. Am. Chem. Soc.*, **1963**, *85*, 683; b: Chatterjee, S. *J. Chem. Soc. B*, **1967**, 1170; c: Sandman, D. J.; Garito, A. F. *J. Org. Chem.*, **1974**, *39*, 1165; d: Maxfield, M. R.; Willi, S. M.; Cowan, D. O.; Bloch, A. N.; Poehler, T. O. *J. Chem. Soc., Chem. Commun.*, **1980**, 947; e: Martin, N.; Hanack, M. *J. Chem. Soc., Chem. Commun.*, **1988**, 1522; f: Hirayama, M.; Seki, A.; Yamashita, Y.; Suzuki, T.; Miyashi, T. *J. Chem. Soc., Chem. Commun.*, **1988**, 490; g: Gerson, F.; Huber, W. *Acc. Chem. Res.*, **1987**, *20*, 85 and references therein.
2. Gerson, F.; Gescheidt, G.; Möckel, R.; Aumüller, A.; Erk, P.; Hünig, S. *Helv. Chim. Acta*, 1988, *71*, 1665.
3. Foster, R. *Molecular Complexes*, Elek Science, London, 1973.
4. Bocelli, G.; Cardellini, L.;De Meo, G.; Ricci, A.; Rizzoli, C.; Tosi, G. *J. Cryst. Spectr.*, 1990, *20*, 561.
5. Candela, G. A.; Swartzendruber, L. J.; Miller, J. S.; Rice, M. J. *J. Am. Chem. Soc.*, 1979, *101*, 2755.
6. Miller, J. S.; Calabrese, J. C.; Ronunelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.*, 1987, *109*, 769.
7. Miller,J . S.; Epstein A. J., *Chem. Br.*, 1994, *30*, 477, and references therein.
8. a: Döpp, D.; Hassan, A. A.; Nour-el-Din, A. M.; Mourad, A. E. in *Organic Free Radicals*, eds. H. Fischer and H. Heimgartner, Springer-Verlag, Berlin, Heidelberg, 1988, p. 41; b: Hssan, E. A. Ph.D. Thesis, University of El-Minia, 1987.
9. Hassan, A. A. *Bull. Soc. Chim. Fr.*, 1991, *128*, 544.
10. Sioda, R. E.; Koski, W. S. *J. Am. Chem. Soc.*, 1967, *89*, 475.
11. Baban, J. A.; Roberts, B. P. *J. Chem. Soc. Perkin Trans. 2*, 1988, 1195.
12. Nelsen, S. F. *J. Am. Chem. Soc.*, 1967, *89*, 5256.
13. a: Alberti, A.; Lucarini, M.; Pedulli, G. F. *Res. Chem. Intermed.*, 1990, *14*, 259; b: Lucarini, M.; Pedulli, G. F.; Alberti, A.; Paradisi, C.; Roffia, S. *J. Chem. Soc., Perkin Trans. 2*, 1993, 2083.
14. a: Russel, G. A.; Whittle, P. R.; Keske, R. G. *J. Am. Chem. Soc.*, 1971, *93*, 1467; b: Russel, G. A.; Janzen, G. *J. Am. Chem. Soc.*, 1962, *84*, 4153; c: Russel, G. A.; Stephens, R. D.; Talati, E. R. *Tetrahedron Letters*, 1965, 1139; d: Russel, G. A.; Weiner, S. A. *J. Org. Chem.*, 1965, *31*, 248.
15. Matsuo, T. *Bull. Chem. Soc. Jpn.*, 1964, *37*, 1844.
16. Andruzzi, R.; Trazza, A.; Greci, L.; Marchetti, A. *Ann. Chim. (Rome)*, 1979, *69*, 583.
17. Andruzzi, R.; Marrosu, G.; Trazza, A.; Kariv-Miller, E. *Electrochim. Acta*, 1986, *31*, 163.
18. Pedulli, G. F.; Tiecco, M.; Alberti, A.; Martelli, G. *J. Chem. Soc., Perkin Trans. 2*, 1973, 1816.

(*Received in UK* 15 *March* 1995; *revised* 9 *May* 1995; *accepted* 12 *May* 1995)