# Stable Free Radicals. Part I. A New Principle governing the Stability of Organic Free Radicals [1]

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The concept of merostabilisation, the stabilisation of free radicals by simultaneous conjugation with electron donor and acceptor groups, is developed by valence bond, MO, and Linnett double quartet theories. The concept is used to rationalise the stabilities of known radicals, and to predict those of new ones, some of which have been synthesised.

BOTH steric hindrance and resonance contribute to the stability of free radicals. In the triphenylmethyl radical [2] the unpaired electron can be delocalised onto C-2, C-4, and C-6 of the phenyl rings. *para*-Nitro-groups allow further delocalisation and result in increased stability;[3] however the unpaired electron cannot reside on C-1, C-3, or C-5 of the aromatic ring unless valence-bond canonical forms carrying a formal positive charge on carbon are involved. Low-energy canonical forms with the unpaired electron on C-1, C-3, or C-5 can be written for radicals of type (1) where electron-donating and electron-accepting substituents interact with the same radical centre.

(1)

(2)

(3)

(4)

(5)
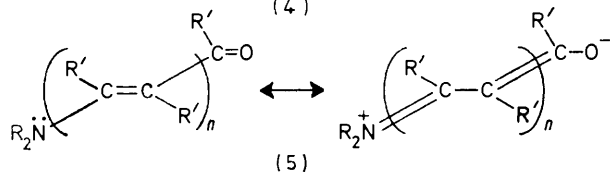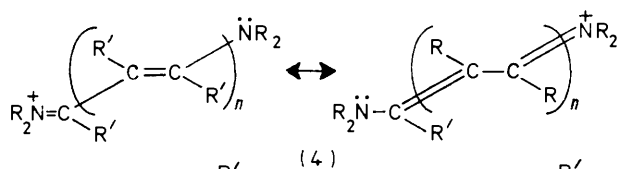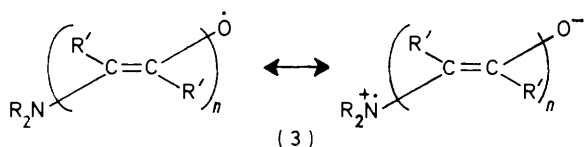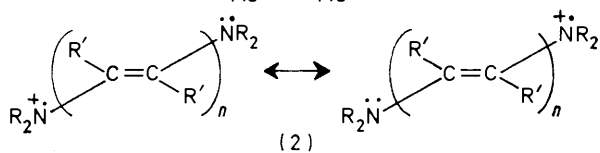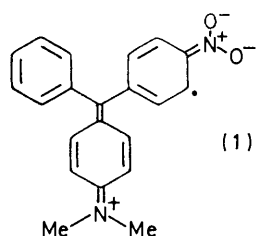
Radicals in which such interaction between different types of substituents can take place should show en-

hanced stability. Radicals such as (1) can be compared to the cations of generalised formula (2) prepared by Hünig and his co-workers.[4] These cations show considerable stability, to disproportionation for example, in part attributable to the complete delocalisation made possible, in this case, by two *similar* substituents. Replacing the $-\overset{+}{\text{N}}\text{R}_2$ group in (2) by $-\overset{\cdot}{\text{O}}$ gives a neutral free radical (3) in which complete delocalisation of the odd electron is again possible. Comparison of the structures (2) and (3) with the generalised structures of the cyanine and merocyanine dyes, (4) and (5), leads us to describe radicals of structure (3) as ' merostabilised.'

Enhanced stability due to merostabilisation should occur in all radicals of formula (6) where $\overset{\cdot}{\text{X}}$ is an electron-donor group such as $\text{R}_2\overset{\cdot}{\text{N}}$, $\text{R}\overset{\cdot}{\text{S}}$ or $\text{R}\overset{\cdot}{\text{O}}$, and $\overset{\cdot}{\text{Y}}$ is a similar group containing one electron less, *e.g.* $\overset{\cdot}{\text{O}}$ or $\overset{\cdot}{\text{N}}\text{R}$.

$n = 0,1,2,3\ldots\ldots$

(6)

(7)

(8)
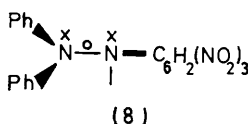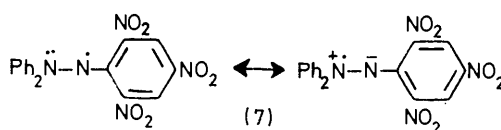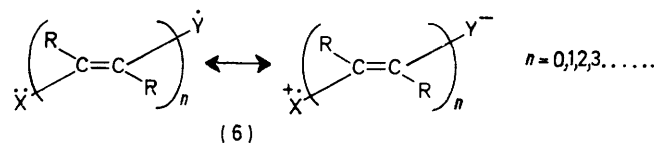
An elegant representation of merostabilisation is provided by Linnett's Double Quartet Theory of electronic structure.[5] By replacing the traditional G. N. Lewis four pairs of valence electrons around an atom by two quartets of electrons of opposite spin, Linnett's theory enables many electronic structures to be succinctly depicted. Linnett divides free radicals into two types. In the first, which includes hydrocarbon radicals such as triphenylmethyl, the odd electron is non-bonding and the radicals are stabilised by resonance and steric hindrance. The second type are the radicals we describe as merostabilised. One of their main canonical forms contains half integral formal charges and three-electron

[1] R. W. Baldock, P. Hudson, A. R. Katritzky, and F. Soti, *Heterocycles*, 1973, 67.
[2] M. Gomberg, *Ber.*, 1900, **33**, 3150.
[3] F. L. Allen and S. Sugden, *J. Chem. Soc.*, 1936, 440.

[4] S. Hünig, *Annalen*, 1964, **676**, 32; S. Hünig, H. J. Friedrich, D. Scheutzow, and W. Brenninger, *Tetrahedron Letters*, 1964, 181.
[5] J. W. Linnett, ' The Electronic Structure of Molecules,' Methuen, London, 1964.

bonds. Thus for diphenylpicrylhydrazyl, instead of the valence bond representation (7), Linnett writes (8) as a major contributing form where circles and crosses represent electrons of opposite spin, and where the light and the heavy lines represent non-coincident and co-incident pairs of electrons, respectively. Dimerisation of radicals of the triphenylmethyl type generally allows gain in stability from two non-bonding electrons forming an electron-pair bond. Merostabilised radicals show no corresponding gain in stability on dimerisation and such radicals thus have less tendency to dimerise. In Linnett's notation our generalised merostabilised radical (6) becomes (9).

(9)
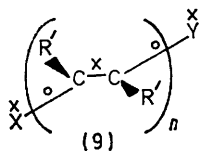
We have sought to express our hypothesis in terms of molecular orbital theory. However, a simple Hückel type approach is not sufficiently sophisticated to re-present this phenomenon, for essentially the same reasons that it fails to predict the existence of negative spin densities.[6] By using the INDO approximation,[7] more support was adduced for merostabilisation, although the results of the calculations show considerable dependence on the geometry chosen.[8] Two criteria, charge separation and spin density spreading, were used to assess the importance of merostabilisation: the effect was found to be more significant for disubstituted methyl radicals (donor and acceptor groups attached directly to the same carbon atom) than for 1,3-di-substituted allyl radicals. The results also support considerable charge separation and spin density spread-ing in substituted pyridinyl radicals.[8]

Other workers have attempted to rationalise the effect of substituents on free radical stability. Walter [9] classifies free radicals empirically as ' O ' or ' S,' in terms of the effect of substituents on spectral properties (chiefly u.v. and e.s.r.), according to whether electron-withdrawing and electron-donating groups have Opposite or the Same effects on the radical properties. In O radicals, which possess a canonical form with a lone pair on the central atom, the effect of substituents is rational-ised by postulating that, where both are possible, delocalisation of a lone pair will be favoured rather than delocalisation of the odd electron.

The ideas presented in this paper were first formulated in 1964,[10] and were developed together with Balaban's similar concepts regarding nitrogen free radicals. Recently, Balaban [11] has pointed out that additional

zwitterionic canonical forms are possible for nitrogen radicals with interacting donor and acceptor groups and has suggested that this should lead to increased stability. The more explicit formulation of these radicals as merostabilised, allowing delocalisation onto all the skeleton atoms, was not enlarged on, but Balaban [12] has successfully predicted the existence of new stable nitrogen radicals.

(10)

(11)   (12)

(13)

(14)

The stability of many other known radicals can be rationalised in terms of merostabilisation. Kosower's radical [13] possesses structures (10). Nitroxides (11) [14] and hydrazyls (12) [15] correspond to (6) with $n = 0$.

[6] A. Streitwieser, jun., ' Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, p. 164.
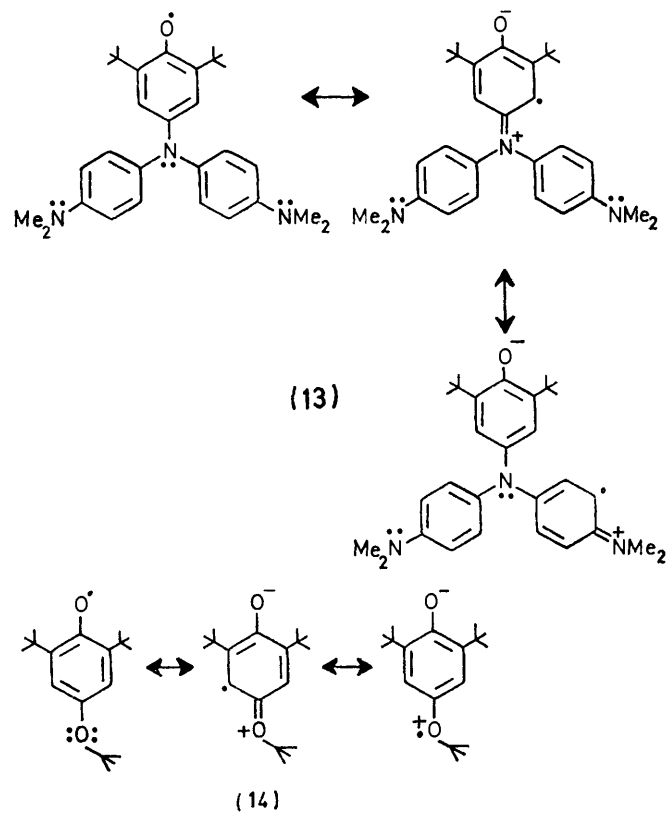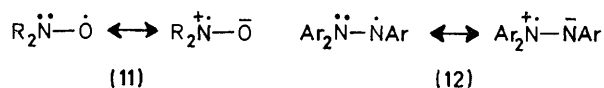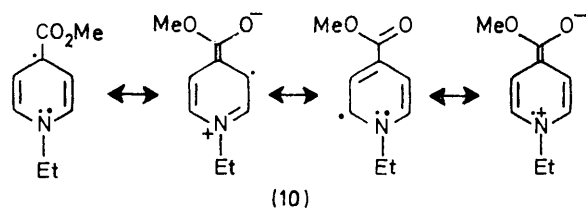
[7] J. A. Pople and D. L. Beveridge, ' Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970, p. 80.

[8] For a full discussion see P. Hudson, Ph.D. Thesis, University of East Anglia, 1973.

[9] R. I. Walter, *J. Amer. Chem. Soc.*, 1966, **88**, 1923.

[10] R. W. Baldock, M.Sc. Thesis, University of East Anglia, 1965.

[11] A. T. Balaban, *Rev. Roumaine Chim.*, 1971, **16**, 725.

[12] N. Negoiţa, R. Baican, and A. T. Balaban, *Tetrahedron Letters*, 1973, 1877; A. T. Balaban and R. Istrătoiu, *ibid.*, p. 1879.

[13] E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, 1964, **86**, 5515.

[14] A. R. Forrester, J. M. Hay, and R. H. Thomson, ' Organic Chemistry of Stable Free Radicals,' Academic Press, London, 1968, ch. 5.

[15] Ref. 14. ch. 4.

The size of the nitrogen coupling constants in pyridinyls, nitroxides, and hydrazyls indicates considerable contributions from charge-separated forms to the resonance hybrid in all these radicals. Zwitterionic forms for certain phenoxyls [16] such as (13) and (14) undoubtedly contribute to the stability of these radicals.

To test the general applicability of the principle of merostabilisation we have predicted the stability of some novel free radicals and attempted to synthesise them. In addition to the known 4-substituted pyridinyls [13,17] [corresponding to (6) with $n = 2$], radicals such as (15) and (16) (corresponding to $n = 1$ and 3, respectively) should be stable: the accompanying paper [18] reports the synthesis of 2,6-disubstituted pyridinyls of type (15). Watanabe, Ikegami, and Seto [19] have recently reported the preparation of 2-methoxycarbonyl-1-methyl-pyridinyl.

We now report pyridinyls of the generalised formula (17). 4-(ββ-Bisethoxycarbonylvinyl)pyridine was prepared by following the method of Rubtsov, Nikitskaya, and Yanina [20] from 4-formylpyridinium chloride and diethyl malonate. Quaternisation with iodomethane and with iodoethane gave the corresponding methiodide and ethiodide as yellow needles. Reduction with zinc dust, or (better) 2% sodium amalgam in acetonitrile, gave 4-(ββ-bisethoxycarbonylvinyl)-1-ethylpyridinyl,

(15)

(16)

(17)

R=Me or Et

X=CO₂Et or COR'
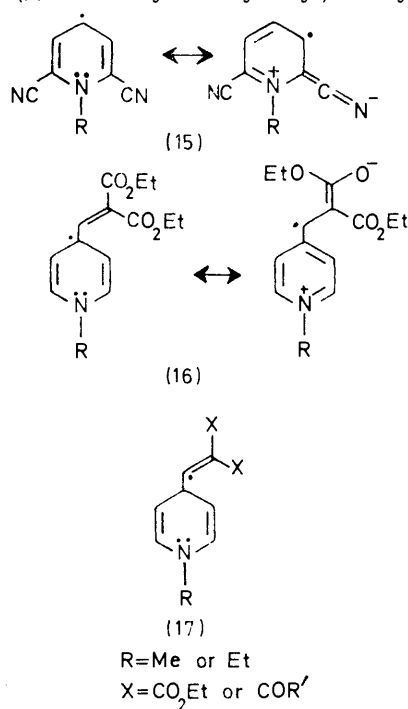
showing e.s.r. spectra of variable resolution (*e.g.* Figure 1). The 1-methyl analogue gives an e.s.r. spectrum with

seven broad lines. The radicals were generally detectable for 12—24 h and in some experiments for much longer. 4-Formylpyridine and indane-1,3-dione gave the diketone (18). Reduction of the corresponding

(18)

(19)a; X = S
    b; X = NH

(20)a; X=S, Ar=Ph
    b; X=NH, Ar=Ph
    c; X=CO, Ar=Ph
    d; X=CO, Ar=4-RC₆H₄
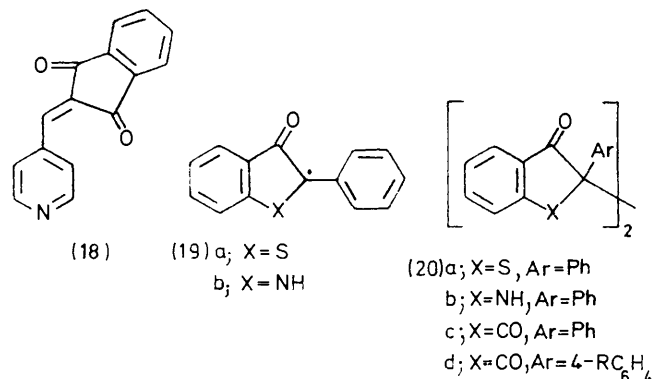
quaternary salts gave radicals showing unresolved e.s.r. spectra.
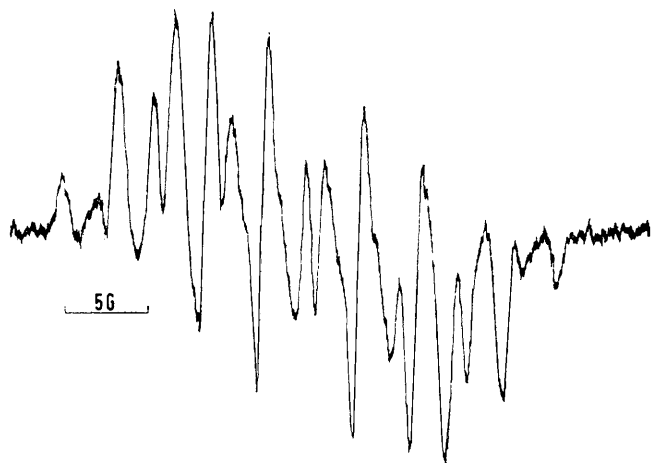
FIGURE 1   E.s.r. spectrum of 1-ethyl-4-(ββ-bisethoxycarbonyl) pyridinyl

Systems of type (19), which should show considerable merostabilisation, have been considered previously in a qualitative way, but no e.s.r. investigation has been reported. Thus colour changes in the dimers (20a) [21,22] and (20b) [23] have been ascribed to dissociation to the monomer (19a) for (20a), but to reversible formation of 2-phenylindol-3-one for (20b). We have prepared the dimers (20a) and (20b) by the published routes and find that readily detectable concentrations of (19a) are formed on heating degassed solutions of (20a) in mesitylene at 40°; at 80—100° well resolved e.s.r. spectra are obtained [Figure 2(a)]. We interpret these spectra in terms of the following coupling scheme: $a_H(1) = 2·83$, $a_H(1) = 2·70$, $a_H(1) = 2·57$, $a_H(2) = 0·90$, $a_H(2) = 0·40$. The computer simulation is shown in Figure 2(b). We assign the largest five couplings to

[16] E. Müller, K. Ley, K. Scheffler, and R. Mayer, *Chem. Ber.*, 1958, **91**, 2682; O. Neunhoeffer and P. Heitmann, *ibid.*, 1963, **96**, 1027.

[17] M. Itoh and S. Nagakura, *Bull. Chem. Soc. Japan*, 1966, **39**, 369.

[18] A. R. Katritzky and F. Soti, following paper.

[19] H. Watanabe, Y. Ikegami, and S. Seto, *Chem. Letters*, 1972, 1107.

[20] M. V. Rubtsov, E. S. Nikitskaya, and A. D. Yanina, *Zhur. obshchei Khim.*, 1953, **23**, 963 (*Chem. Abs.*, 1954, **48**, 8781e).

[21] L. Kalb and J. Bayer, *Chem. Ber.*, 1913, **46**, 3879.

[22] *Cf.* also A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 1945, 657; 1949, 889; A. Mustafa and A. M. Islam, *ibid.*, 1951, 1616.

[23] L. Kalb and J. Bayer, *Ber.*, 1912, **45**, 2150.

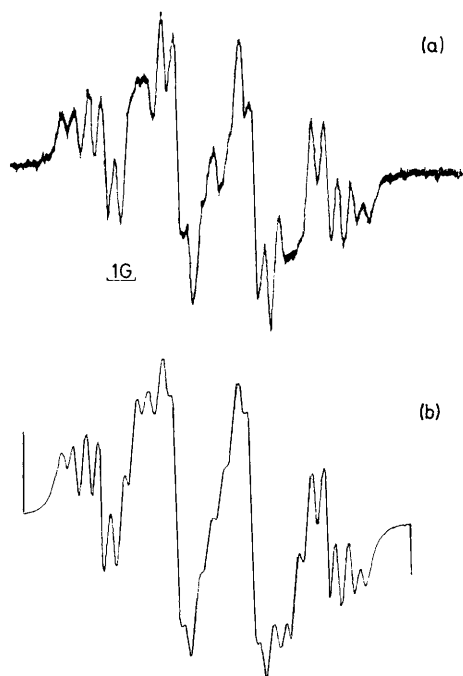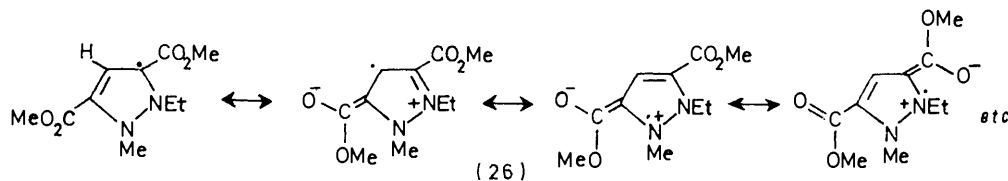the hydrogen atoms of the phenyl group and the two smallest to two of the hydrogen atoms of the benzo-ring,

FIGURE 2 (a) E.s.r. spectrum of the radical (19a); (b) computer simulation

in agreement with the work of de Jongh and his school.[24,25] Possible complications from negative spin densities and the absence of comparative data for (21) make difficult the quantitative assessment of the contribution of the form (22).

The dissociation of the dimer (20a) to (19a) is reversible. However although the dimer (20b) produces the radical (19b) at 40°, this decays irreversibly at higher temperatures and no well resolved e.s.r. spectrum was obtained. It is significant that Beringer *et al.*[26] state that the dimer (20c) produces the radical (21) only above 100°: merostabilisation is absent in (21). Further, Stradins *et al.*[27] found e.s.r. evidence to suggest

3,5-dicarboxylic acid with diazomethane gave the *N*-methyl diester (24), which was quaternised with triethyl-oxonium fluoroborate.[28] Reduction of the fluoroborate

with potassium in 1,2-dimethoxyethane gave a green solution with an e.s.r. signal showing five main lines

SCHEME 1

each split into two. The lifetime is of the order of 10—20 min at both 25 and —80°. Stabilisation of type (26) affects the ester group conjugation, which reduces the importance of such forms.
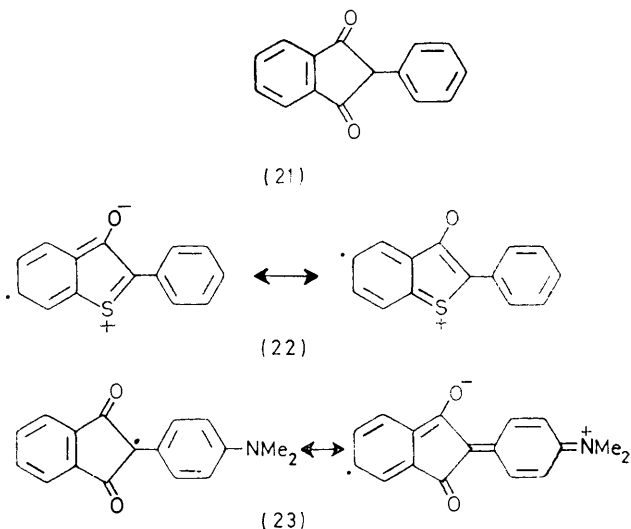

that of the *para*-substituted phenyl dimers (20d), only the *p*-dimethylamino-compound underwent detectable dissociation, to the radical (23) which is merostabilised.

The pyrazolyl radical (25) with a lifetime of a few minutes was prepared according to Scheme 1. Pyrazole-
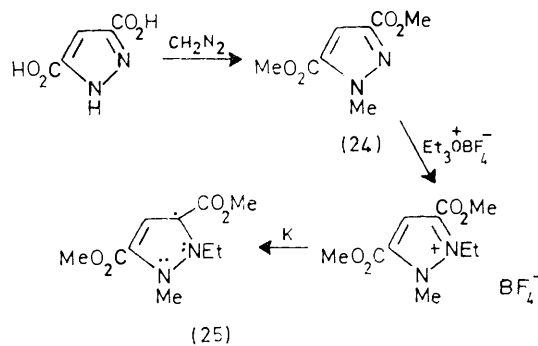
Ethyl methylcarbamate and *o*-nitrobenzoyl chloride gave ethyl *N*-methyl-*N*-*o*-nitrobenzoylcarbamate (27), which was cyclised (*cf.* ref. 29) to 1,2,3,4-tetrahydro-1-hydroxy-3-methyl-2,4-dioxoquinazoline (28), converted

[24] H. A. P. de Jongh, C. R. H. I. de Jongh, and W. J. Mijs, *J. Org. Chem.*, 1971, **36**, 3160; H. A. P. de Jongh, C. R. H. I. de Jongh, H. J. M. Sinnige, W. J. de Klein, W. G. B. Huysmans, W. J. Mijs, W. J. van den Hoek, and J. Smidt, *ibid.*, 1972, **37**, 1960.

[25] W. J. van den Hoek, B. A. C. Rousseeuw, J. Smidt, W. G. B. Huysmans, and W. J. Mijs, *Chem. Phys. Letters*, 1972, **13**, 429.

[26] F. M. Beringer, S. A. Galton, and S. J. Huang, *Tetrahedron*, 1963, **19**, 809.

[27] J. Stradins, I. Tutane, O. Neiland, and G. Vanags, *Doklady Akad. Nauk S.S.S.R.*, 1966, **166**, 631 (*Doklady Chem.*, 1966, **166**, 140).

[28] T. J. Curphey, *J. Amer. Chem. Soc.*, 1965, **87**, 2063.

[29] R. T. Coutts, D. Noble, and D. G. Wibberley, *J. Pharm. Pharmacol.*, 1964, **16**, 773.

into the expected nitroxide radical (29) by PbO_2. Merostabilisation in this radical is illustrated by the
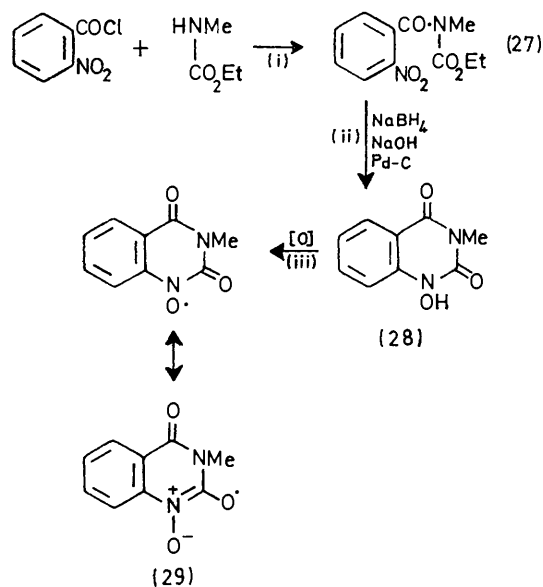
SCHEME 2

canonical forms shown (29). The e.s.r. spectrum (Figure 3) contains nine lines corresponding to the two nitrogen atoms of the radical ($a_N = 6\cdot12$, $a_N \simeq 2\cdot1$ G); the hydrogen atoms cause only line broadening.

We also attempted to prepare simple merostabilised benzyl radicals. Mono- and di-arylmethyl radicals are generally of low stability unless stabilised by bulky
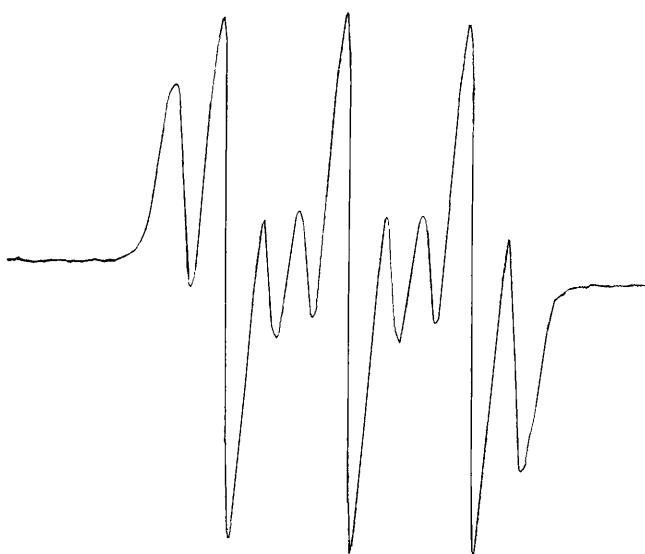

FIGURE 3   E.s.r. spectrum of 1,2,3,4-tetrahydro-3-methyl-2,4-dioxoquinazoline N-oxyl (29)

ortho-substituents in the aromatic ring(s).[30] There is evidence for the existence of radicals such as (30) [31]

[30] H. S. Jarrett and G. J. Sloan, J. Chem. Phys., 1954, 22, 1783; K. H. Fleurke and W. Th. Nauta, Rec. Trav. chim., 1965, 84, 1059; M. Ballester and J. Riera, J. Amer. Chem. Soc., 1964, 86, 4505.

and (31) [32] as transient intermediates and recently de Jongh et al.[24,25] have obtained radicals such as (32) and (33) (observed by e.s.r.) by heating the corresponding dimer. None of these radicals possesses significant stability at room temperature. In the case of the radicals (32) it is noticeable that for the case where R = MeO the meta-H coupling constant ($0\cdot87$ G) is much less than those for the other four radicals studied ($1\cdot25$—$1\cdot50$ G). This reduction in the size of the negative spin density on the meta-carbon atom is good evidence for contributions from forms such as (34) which will not be favoured when R is not an electron-donating group. We tried to prepare merostabilised benzyl radicals of formula (35) but attempts to oxidise the anions of α-dialkylaminoarylacetonitriles with iodine gave cation radicals (36).
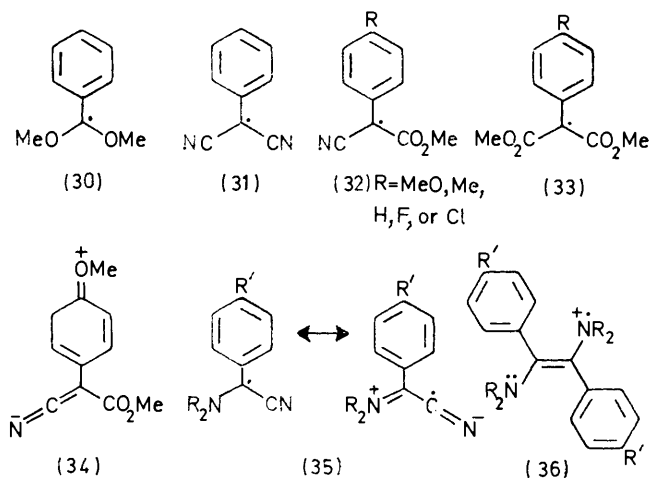
EXPERIMENTAL

4-($\beta\beta$-Bisethoxycarbonylvinyl)-1-methylpyridinium Iodide. —4-($\beta\beta$-Bisethoxycarbonylvinyl)pyridine,[20] b.p. 129—131° at $0\cdot4$ mmHg (lit.,[20] 176—178° at 7 mmHg) ($0\cdot30$ g), heated with iodomethane (3 ml) for 3 h, gave the methiodide ($0\cdot27$ g, $57\cdot3\%$), yellow needles (from EtOH), m.p. 175—177° (Found: C, $43\cdot2$; H, $5\cdot1$; I, $32\cdot8$; N, $3\cdot4$. $C_{14}H_{18}INO_4$ requires C, $43\cdot0$; H, $4\cdot6$; I, $32\cdot5$; N, $3\cdot6\%$); τ (D_2O) $1\cdot37$ (2H, d), $2\cdot04$ (3H, s), $5\cdot2$—$6\cdot0$ (7H, m), $8\cdot58$ (3H, t), and $8\cdot69$ (3H, t).

The corresponding ethiodide ($0\cdot89$ g, $73\cdot3\%$) formed yellow needles (from EtOH), m.p. 145—146° (Found: C, $44\cdot5$; H, $5\cdot1$; I, $31\cdot2$; N, $3\cdot7$. $C_{15}H_{20}INO_4$ requires C, $44\cdot4$; H, $4\cdot9$; I, $31\cdot4$; N, $3\cdot5\%$); τ (D_2O) $0\cdot86$ (2H, d), $1\cdot76$ (3H, m), $5\cdot16$ (2H, q), $5\cdot46$ (2H, q), $5\cdot51$ (2H, q), $8\cdot20$ (3H, t), $8\cdot51$ (3H, t), and $8\cdot65$ (3H, t).

2-(4-Pyridylmethylene)indane-1,3-dione (18).—Piperidine ($0\cdot1$ g), 4-formylpyridine ($1\cdot07$ g, $0\cdot01$ mol), indane-1,3-dione ($1\cdot46$ g, $0\cdot01$ mol), and 95% EtOH (25 ml) were stirred for 30 min and kept at 0° for 15 h. The dione separated, and more was obtained by concentration; it crystallised from EtOH as yellowish-green needles ($1\cdot32$ g, $56\cdot2\%$), m.p. 167—169° (Found: C, $76\cdot6$; H, $4\cdot0$; N, $6\cdot3$. Calc. for $C_{15}H_9NO_2$: C, $76\cdot6$; H, $3\cdot8$; N, $6\cdot0\%$); τ ($CDCl_3$) $1\cdot23$ (2H, d) and $1\cdot86$—$2\cdot28$ (7H, m). The methiodide crystallised from MeCN–EtOAc in purple microcrystals

[31] R. L. Huang and K. H. Lee, Tetrahedron Letters, 1963, 711.
[32] H. D. Hartzler, J. Org. Chem., 1966, 31, 2654.

(0·118 g, 31·3%), m.p. 218—220° (Found: N, 3·6. $C_{16}H_{12}INO_2$ requires N, 3·7%).

2,2'-Diphenyl-2,2'-bibenzo[b]thiophen-3,3'-dione [21] had m.p. 234° (lit.,[21] 231°). 2,2'-Diphenyl-2,2'-bi-indole-3,3'-dione [33] had m.p. 180—181° (lit.,[23,34] 180—182°).

2-*Ethyl*-3,5-*bismethoxycarbonyl*-1-*methylpyrazolium Fluoroborate*.—3,5-Bismethoxycarbonyl-1-methylpyrazole [35] (24) (0·32 g), triethyloxonium fluoroborate (3 g), and ethylene chloride (15 ml) (dry nitrogen glove-box) were heated under reflux for 30 h. Addition of ether (15 ml) gave the *fluoroborate* (0·37 g, 75%), which crystallised from toluene–ethylene dichloride as plates, m.p. 182—185° (Found: C, 38·25; H, 5·07. $C_{10}H_{15}BF_4N_2O_4$ requires C, 38·25; H, 4·77); τ ($CF_3 \cdot CO_2H$) 2·2 (1H, s), 4·8 (2H, q, J 7·2 Hz), 5·33 (3H, s), 5·85 (6H, s), and 8·34 (3H, t, J 7·2 Hz); ν (Nujol) 1735 (C=O) cm⁻¹.

1-*Hydroxy*-3-*methylquinazoline*-2(1H),4(3H)-*dione* (28).— o-Nitrobenzoyl chloride (0·025 mol) and ethyl methylcarbamate (0·03 mol) were heated for 1 h at 190°. Ether (50 ml) was added and the solution was washed with water (5 × 10 ml), aqueous 2M-Na_2CO_3 (5%; 5 × 10 ml), and water again (2 × 10 ml), dried, decolourised, and evaporated to give crude ethyl N-methyl-N-o-nitrobenzoylcarbamate as a yellow oil (3·15 g, 50%).

NaBH₄ (0·0025 mol), aqueous NaOH (2%; 5 ml), and Pd–C (10%, 0·05 g) were stirred at 0° under nitrogen. Ethyl N-methyl-N-o-nitrobenzoylcarbamate (0·01 mol) in dioxan (10 ml) was added dropwise during 5 min. After further addition of NaBH₄ (0·0025 mol) the suspension was stirred at 20° for 1·5 h. After filtration, water (25 ml) was added to the filtrate and the whole extracted with ether (3 × 25 ml). The extract was dried and evaporated to give starting material (1·16 g, 46%). The aqueous solution was acidified with HCl (2 ml), to give the *quinazolinedione* as white needles (0·245 g, 24%), m.p. 254—257° (from EtOH) (Found: C, 55·9; H, 4·5; N, 14·6. $C_9H_8N_2O_3$ requires C, 56·3; H, 4·2; N, 14·6%); τ [(CD₃)₂SO] −1·36 (1H, s), 1·8—2·9 (4H, m), and 6·67 (3H, s).

α-*Aminoacetonitriles*.—The following were prepared by the method of Morris and Hauser: [36] α-(N-*methylanilino*)-*phenylacetonitrile* (2·48 g, 11·2%), needles, m.p. 69—70° [from light petroleum (b.p. 40—60°)], b.p. 131—132° at 0·35 mmHg (Found: C, 81·0; H, 6·3; N, 12·3. $C_{15}H_{14}N_2$ requires C, 81·0; H, 6·3; N, 12·6%); τ (CCl₄) 2·30—3·30 (10H, m), 4·37 (1H, s), and 7·39 (3H, s); α-(N-*n-butyl-anilino*)*phenylacetonitrile* (3·7 g, 14·0%), needles, m.p. 49—51° [from light petroleum (b.p. 40—60°)] (Found: C, 81·8; H, 7·6; N, 10·6. $C_{18}H_{20}N_2$ requires C, 81·8; H, 7·6; N, 10·6%); τ (CCl₄) 2·35—3·25 (10H, m), 4·52 (1H, s), 6·93 (2H, m), and 8·50—9·40 (7H, m); α-(N-*methyl*-N-*ethylamino*)-*phenylacetonitrile* (3·24 g), oil, b.p. 80—83° at 1·0 mmHg (Found: C, 75·6; H, 8·3; N, 16·1. $C_{11}H_{14}N_2$ requires C, 75·9; H, 8·0; N, 16·1%); n_D^{21} 1·5112; τ (CCl₄) 2·35—2·75 (5H, m), 5·23 (1H, s), 7·48 (2H, q), 7·84 (3H, s), and 8·90 (3H, t); α-*dimethylamino*-2,4,6-*trimethylphenylacetonitrile* (0·72 g, 7·3%), oil, b.p. 93—95° at 0·4 mmHg (Found: C, 77·0; H, 8·9; N, 13·5. $C_{13}H_{18}N_2$ requires C, 77·2; H, 8·9; N, 13·9%); n_D^{16} 1·5264; τ (CCl₄) 3·25 (2H, s), 5·60 (1H, s), 7·59 (6H, s), 7·75 (6H, s), and 7·78 (3H, s).

The following were made by adaptation of the literature methods quoted: α-(*diphenylamino*)*phenylacetonitrile* [37] (5·8 g, 41%), m.p. 100—102°, as prisms (from MeOH) (Found: C, 84·3; H, 5·7; N, 9·8. $C_{20}H_{16}N_2$ requires C, 84·5; H, 5·6; N, 9·9%); τ (CDCl₃) 2·4—3·2 (15H, m) and 3·97 (1H, s); 2-*dimethylamino*-3,3-*dimethylbutyronitrile* [38] (2·0 g, 50%), oil, b.p. 60—62° at 12 mmHg (Found: C, 68·5; H, 11·9; N, 19·7. $C_8H_{16}N_2$ requires C, 68·6; H, 11·4; N, 20·0%); τ (CCl₄) 6·99 (1H, s), 7·72 (6H, s), and 8·98 (9H, s); n_D^{20} 1·4288.

Preparation of Radicals.—For the pyridinyl and the pyrazolyl, essentially the technique of ref. 18 was used. The dissociation of the dimer was followed in degassed solutions in mesitylene. The quinazoline nitroxide radical was prepared by oxidation with PbO₂ in dioxan with exclusion of oxygen.

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