Semidiones. X. Semidione Radical Anions Derived from Indan-2,3-dione, Coumaran-2,3-dione, Thianaphthalenequinone, Isatin, and N-Hydroxyisatin. Nitroxide Radicals Derived from Isatin, Dioxindole, Oxindole, and Other Indole Derivatives[1]

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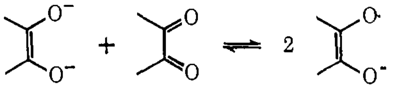
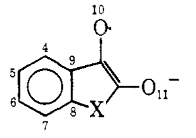
Abstract: Indan-1,2-dione, coumaran-2,3-dione, thianaphthalenequinone, isatin, N-methylisatin, and N-hydroxyisatin can be reduced to the semidiones by treatment with the enolate anion of propiophenone in dimethyl sulfoxide solution. Nitroxides are readily prepared from N-hydroxyisatin, N-hydroxyoxindole, and N-hydroxydioxindole by treatment with lead dioxide in dioxane. Another nitroxide formed spontaneously from N-hydroxyisatin in basic dimethyl sulfoxide solutions in the presence of oxygen is assigned the structure of a monoanion of isodioxindole nitroxide (**4b**). Isatin and N-hydroxyisatin radical monoanions exist in equilibrium with the radical dianions which can be detected at high basicities. N,N-Dimethylindigo is readily converted in basic dimethyl sulfoxide solution to the N-methylisatin radical anion. Oxidation of 1-hydroxy-2-phenylindole with lead tetraacetate or *p*-nitroperbenzoic acid led to a radical assigned the 2-phenyl-2-hydroxyindoxyl nitroxide structure (**15a**) while oxidation with lead dioxide or diethyl azoformate yielded a dimeric nitroxide, 1-oxy-1′-hydroxy-2,2′-diphenyl-3,3′-biindole. Diisatogen (1,1′-dioxy-2,2′-bi-3*H*-indole-3,3′-dione) was converted into a nitroxide (1,1′-dioxy-2-hydro-2-hydroxy-2,2′-bi-3*H*-indole-3,3′-dione) by refluxing in mesitylene solution. Under basic conditions in the presence of oxygen N-hydroxyisatin, N-hydroxydioxindole, or the diisatogen can also be converted to *o*-carboxyphenyl nitroxide or *o*-carboxynitrosobenzene radical anion (**5a** ⇄ **5b**). The literature is examined and it is argued that radicals with structures **5a** and **15** have been observed previously in the reaction of 2-phenylisatogen.

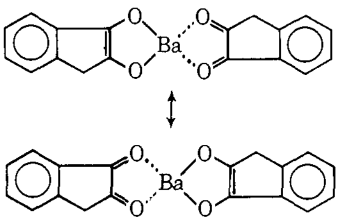
Indan-1,2-semidione (**1a**) is a remarkably stable semidione that can be observed in aqueous solution. Our interest in **1a** was stimulated by our previous work on ninhydrinsemidione (**1b**)[4] and by the report of Criegee and Klonk[5] that barium hydroxide and a mixture of indan-1,2-dione and 2-acetoxy-1-indanone yielded a blue powder (pyrophoric in air) to which structure **2** was assigned. We have found that the blue powder has little or no esr absorption but yielded the esr spectrum of **1a** when dissolved in a solvent. Criegee's formulation of the blue solid as a diamagnetic molecule seems to be substantiated.[6] In solution the dianions of the enediol undergo a comproportionation reaction with the diketone to yield the radical anion.



We have also examined by esr spectroscopy the preparation of semidiones **1c**–**1k**.



1a, X = CH_2
1b, X = C=O
1c, X = $C(CH_3)_2$
1d, X = $C(OCH_3)_2$
1e, X = O
1f, X = S
1g, X = NCH_3
1h, X = NH
1i, X = N^-
1j, X = NOH
1k, X = NO^-



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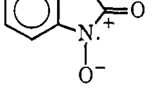

3a, X = CO
3b, X = CH(OH)
3c, X = CH_2

Our investigation of **1j** and **1k** forced us to consider the nitroxides derived from isatin, dioxindole, and oxindole (**3a**–**3c**). In basic solution the nitroxide **3b** could yield a number of monoanions isomeric with **1j**. We present evidence supporting structure **4b** and eliminating **4a**, **4c**–**4e** for a radical anion produced from N-hydroxyisatin in the presence of oxygen. All attempts to produce a dianion radical from **3b** have led to the ring opened products, **5a** ⇄ **5b**. Radicals derived from isatogens[7] (**6**) were also examined as well

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(1) Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XVII. This work was supported by National Science Foundation Grant No. GP-6402.

(2) National Defense Education Act Predoctoral Fellow, 1965–1968.

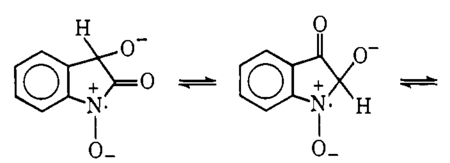
(3) North Atlantic Treaty Organization Postdoctoral Fellow, 1967–1968.

(4) G. A. Russell and M. C. Young, *J. Amer. Chem. Soc.*, **88**, 2007 (1966).

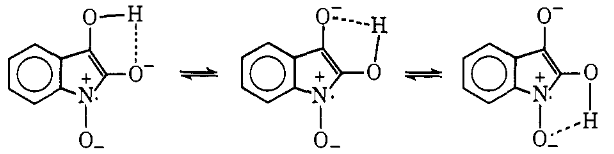
(5) R. Criegee and K. Klonk, *Justus Liebigs Ann. Chem.*, **564**, 1 (1949).

(6) The green calcium salts of semiquinones are also diamagnetic in the solid state: L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, 70, 624 (1948).

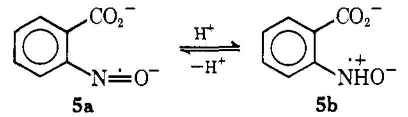
(7) L. Lunazzi, G. F. Pedulli, G. Maccagnasi, and A. Mangini, *J. Chem. Soc., B*, 1072 (1967).



4a **4b**

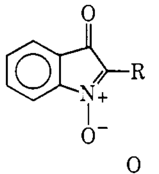


4c **4d** **4e**

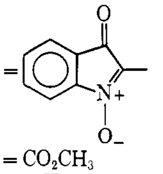


5a **5b**

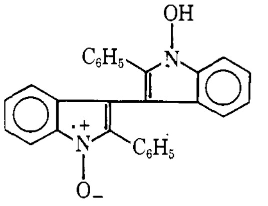
as the nitroxide **7** obtainable from 1,1′-dioxy-2,2′-diphenyl-$\Delta^{3,3'}$-bi-3*H*-indole.[8,9]



6a, R =



b, R = CO_2CH_3
c, R = C_6H_5



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Results and Discussion

Indan-1,2-dione or 2-acetoxy-1-indanone spontaneously yield **1a** when dissolved in deoxygenated solvents containing potassium *t*-butoxide. The highest yield of **1a** was observed when equal amounts of the dione and α-acetoxy ketone were employed. Radical anion **1a** can also be obtained by the exposure of 1-indanone to air in basic DMSO solution. Surprisingly **1a** can also be obtained by the reduction of ninhydrin by zinc in concentrated aqueous base.[4] The spectrum of **1a** has been previously given (see Figure 3, ref 4). In water **1a** had hyperfine splitting constants (hfsc) of a^{H} = 3.00 G (3 H), 2.80 (1 H), and 0.77 (2 H). In D_2O two of the 3-G hydrogens were readily exchanged to give a^{D} = 0.445, $a^{\mathrm{H}}/a^{\mathrm{D}}$ = 6.75. In DMSO the hfsc were $a_{\mathrm{CH_2}}{}^{\mathrm{H}}$ = 2.64, $a_{\mathrm{CH}}{}^{\mathrm{H}}$ = 2.95, 2.83, 0.73, and 0.56 G. The spin distribution is somewhat different than for 1-phenylpropane-1,2-semidione where $a_{\mathrm{CH_3}}{}^{\mathrm{H}}$ = 3.43, $a_o{}^{\mathrm{H}}$ = 1.6, $a_p{}^{\mathrm{H}}$ = 1.8, and $a_m{}^{\mathrm{H}}$ = 0.5 G were observed.[10] 3,3-Dimethylindan-1,2-dione, 3,3-dimethoxyindan-1,2-dione, coumaran-2,3-dione, thianaphthenequinone, and N-methylisatin were reduced to the corresponding semidiones (Figure 1) whose hfsc are given in Table I.

The larger values of $a_{\mathrm{aromatic}}{}^{\mathrm{H}}$ are undoubtedly associated with the hydrogen atoms at C-4 and C-6 in **1a–1g**. In Table II are given spin densities (ρ_{C}) calculated by the McLachlan MO method[11] and the

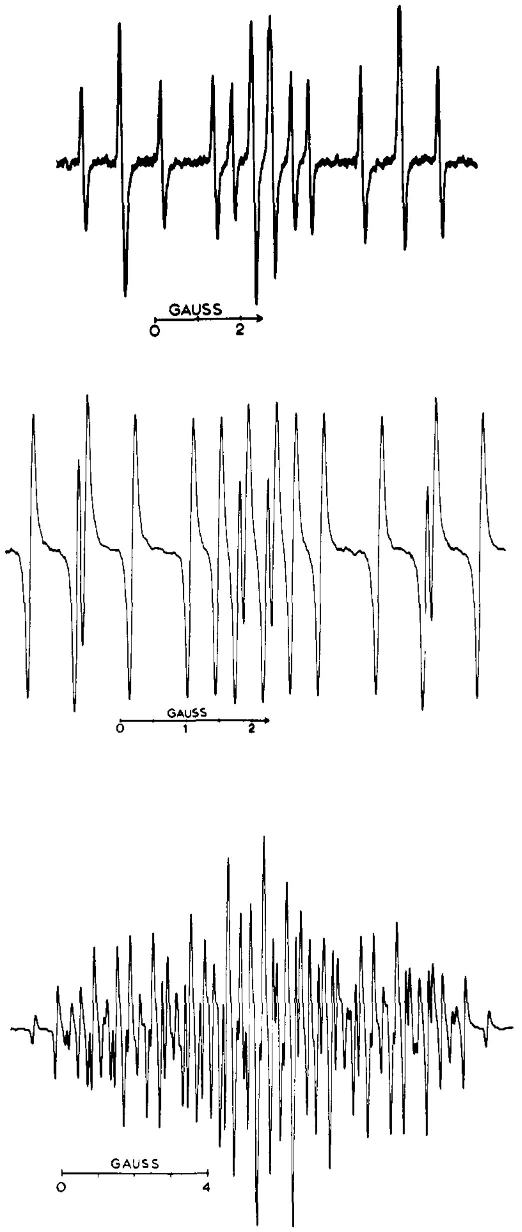

Figure 1. Esr first-derivative spectra of potassium salts of **1e**, **1f**, and **1g** in dimethyl sulfoxide solution in 30°: top, coumaran-2,-3-semidione; middle, thianaphthalene semiquinone; bottom, N-methylisatinsemidione. The spectra are excellently reproduced by the addition of Lorentzian peaks with a 0.15-G half-width.

Table I. Hyperfine Splitting Constants (G) of **1** in DMSO at 30°

X =	$a_{\mathrm{aromatic}}{}^{\mathrm{H}}$	Other hfsc
1a, CH_2	2.95, 2.83, 0.73, 0.56	$a_{\mathrm{CH_2}}{}^{\mathrm{H}}$ = 2.62
1d, $C(OCH_3)_2$	2.45, 2.45, 0.65, 0.13	$a_{\mathrm{CH_3}}{}^{\mathrm{H}}$ = 0.13
1c, $C(CH_3)_2$	2.87, 2.75, 0.81, 0.47	$a_{\mathrm{CH_3}}{}^{\mathrm{H}}$ = 0.33
1b, C═O[a]	0.95, 0.95, 0.95, 0.95	
1e, O	3.44, 3.04, 0.91, 0.91	
1f, S	2.86, 2.43, 0.82, 0.70	
1g, NCH_3	3.86, 2.94, 1.00, 1.00	a^{N} = 0.90, $a_{\mathrm{CH_3}}{}^{\mathrm{H}}$ = 0.63
1h, NH	3.73, 3.17, 1.00, 0.92	a^{N} = 1.06, $a_{\mathrm{NH}}{}^{\mathrm{H}}$ = 0.19
1i, N^-	4.23, 3.40, 0.99, 0.99	a^{N} = 0.53
1j, NOH	3.74, 2.91, 0.70, 0.70	a^{N} = 0.35, $a_{\mathrm{OH}}{}^{\mathrm{H}}$ = 0.33
1k, NO^-	3.67, 2.74, 1.02, 0.64	a^{N} = 0.17

[a] Reference 4.

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(8) M. Colonna and P. Bruni, *Gazz. Chim. Ital.*, **94**, 1448 (1964); M. Colonna, P. Bruni, and L. Marchetti, *Boll. Sci. Fac. Chim. Ind., Bologna*, **25**, 95 (1967).

(9) A. R. Forrester, R. H. Thomson, and G. R. Luckhurst, *J. Chem. Soc. B*, 1311 (1968).

(10) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Amer. Chem. Soc.*, **88**, 1998 (1966).

(11) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

Table II. HMO Computed McLachlan Spin Density, ρ, for **1**[a]

Position	X = CH_2 Calcd ρ	X = CH_2 Exptl $\lvert\rho\rvert$	X = O Calcd ρ	X = O Exptl $\lvert\rho\rvert$	X = S Calcd ρ	X = S Exptl $\lvert\rho\rvert$	X = NCH_3 Calcd ρ	X = NCH_3 Exptl $\lvert\rho\rvert$	X = CO Calcd ρ	X = CO Exptl $\lvert\rho\rvert$
1	0		−0.008		−0.032		−0.012			
2	0.378		0.324		0.334		0.315			
3	0.333		0.382		0.375		0.38			
4	0.079	0.148	0.079	0.143	0.072	0.101	0.077	0.150	−0.0005	0.040
5	−0.039	0.023	−0.038	0.038	−0.039	0.029	−0.038	0.042	0.021	0.040
6	0.055	0.123	0.067	0.127	0.074	0.110	0.071	0.126	0.021	0.040
7	−0.039	0.030	−0.045	0.038	−0.051	0.034	−0.047	0.042	−0.0005	0.040
8	0.070		0.091		0.101		0.096			
9	0.059		−0.056		−0.048		−0.055			
10	0.113		0.089		0.100		0.090			
11	0.100		0.117		0.113		0.116			

[a] $\alpha_0(C{=}O) = \alpha_C + 1.8\beta_{CC}$; $\alpha_N = \alpha_C + 1.5\beta_{CC}$; $\alpha_O(C–O) = \alpha_C + 2.0\beta_{CC}$; $\alpha_S = \alpha_C + 1.0\beta_{CC}$; $\beta_{C=N} = \beta_{C=O} = 0.8\beta_{CC}$; $\beta_{C=O} = \beta_{CC}$; $\beta_{C=S} = 0.566\beta_{CC}$. The X atom has been numbered position 1 in these indan derivatives.

McConnell equation,[12] $a^H = -24\rho_C$. The molecular orbital calculations also explain the surprisingly low value of $a_{CH_2}{}^H$ in **1a** (2.64 G) compared with the methyl group in 1-phenylpropane-1,2-semidione ($a_{CH_3}{}^H$ = 3.43 G). In **1a** one might have expected a larger hyperconjugation interaction according to the formula $a^H = \rho_C B\langle\cos^2\theta\rangle$.[13] For the freely rotating methyl group in 1-phenylpropane-1,2-semidione $\langle\cos^2\theta\rangle$ is 0.5, while in rigid **1a** θ is 30° ($\cos^2\theta = 0.8$). Moreover, in **1a** spin density is appreciable at both C-2 and C-8. What is involved here is undoubtedly connected with the orbital symmetries for the coefficients, for the HOMO of **1a** have different signs at C-2 and C-8. A Hückel calculation with $\alpha_O = \alpha_C + 1.8\beta_{CC}$ and $\beta_{CO} = \beta_{CC}$ yields $c_2 = 0.55$ and $c_8 = -0.26$ for ψ_6 of **1a**. Since the hfs is given by $a^H = B(c_2 + c_8)^2\cos^2\theta$,[14] it follows that the ratio of $a_{CH_2}{}^H$ in **1a** and $a_{CH_3}{}^H$ in 1-phenylpropane-1,2-semidione should be $(0.55–0.26)^2(0.8)/(0.55)^2(0.5) = 0.45$; observed 2.64/3.64 = 0.73.

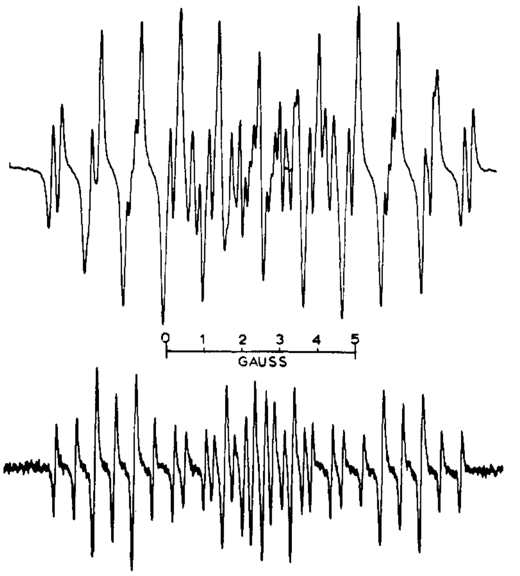


Figure 2. Esr first-derivative spectra of the potassium salts of the semidiones **1h** and **1i**: top, isatinsemidione in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%); bottom, isatinsemidione dianion in dimethyl sulfoxide.

Polarographic reduction potentials were measured for N-methylisatin, coumaran-2,3-dione, and thianaphthenequinone in DMSO solution. Nernst plots of E *vs.* log $(i/i_d - i)$ for the first reduction wave gave linear plots with a slope of 1.0 indicative of a reversible one-electron reduction. Table III lists the observed half-wave potential and the Hückel energy of the LUMO in the diketone.

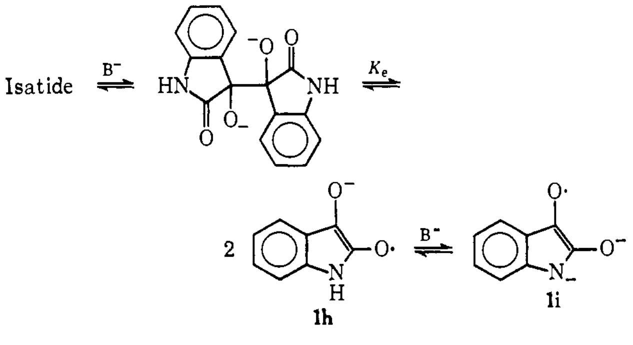
Table III. Reduction Potentials and Energy of LUMO of 1,2-Diketones

Compound	E_{calcd} (β)	$-E_{1/2}$ (V)[a]
N-Methylisatin	0.221	0.88
Coumaran-2,3-dione	0.223	0.65
Thianaphthenequinone	0.226	0.54

[a] In 0.1 *M* solution of tetra-*n*-propylammonium perchlorate in dimethyl sulfoxide *vs.* a saturated calomel electrode.

The data of Table III give a fair correlation with the relationship, $E_{1/2} = -1.15 + 2.5(E_{calcd})$ proposed previously for the reduction of vicinal ketones.[15]

Isatide when treated with base gave an appreciable concentration of **1h** or **1i** depending on the basicity. The spectra were quite different and were readily distinguishable (Figure 2). The dissociation of isatide is similar to the dissociation of hydrindantin and alloxantin described previously.[3] The isatin radical anions were also produced from isatin by treatment with DMSO containing potassium *t*-butoxide or with a mixture of potassium *t*-butoxide and propiophenone.[16] Another route to the isatin radical anion was the



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(12) H. M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956).

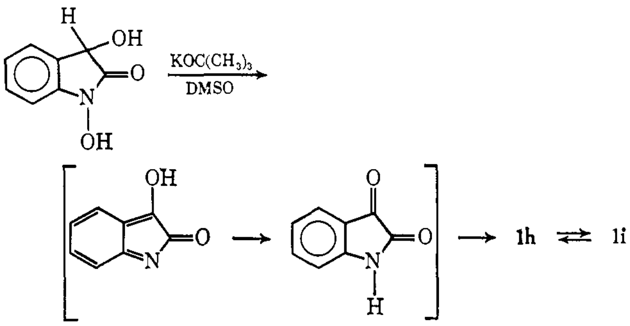
(13) M. C. R. Symons, *J. Chem. Soc.*, 277 (1959).

(14) D. H. Whiffen, *Mol. Phys.*, **6**, 224 (1963).

(15) G. A. Russell and S. A. Weiner, *J. Amer. Chem. Soc.*, **89**, 6623 (1967).

(16) For numerous examples of the use of the enolate anion of propiophenone as a one-electron reducing agent, see G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).

reaction of N-hydroxydioxindole with potassium *t*-butoxide in DMSO solution. Here the elimination of water to yield isatin must be occurring. Semidione **1i**



was observed in DMSO and **1h** in DMSO (80%)-*t*-butyl alcohol (20%) solution. Both oxindole and dioxindole reacted with a trace of oxygen in DMSO solutions of potassium *t*-butoxide to yield **1h** or **1i**.

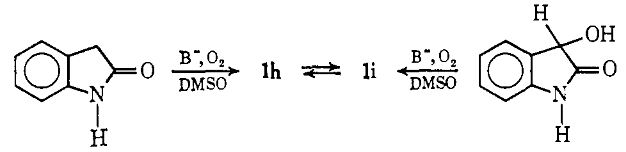
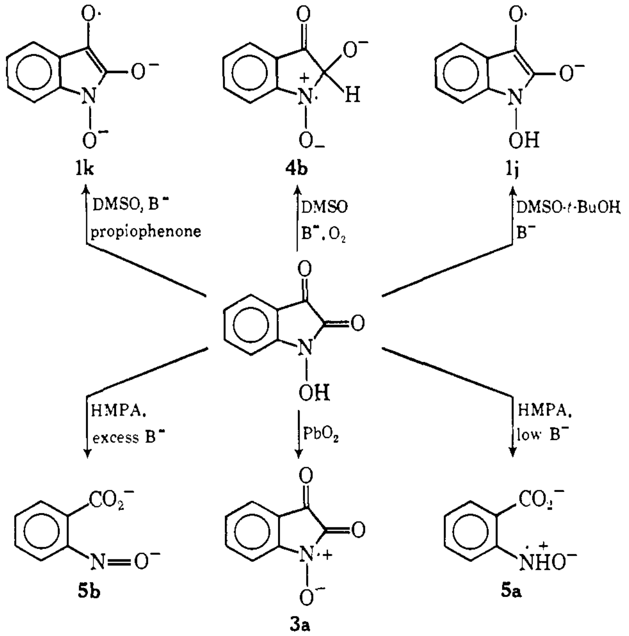
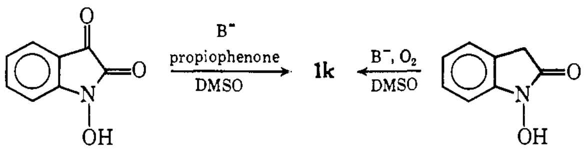


Chart I





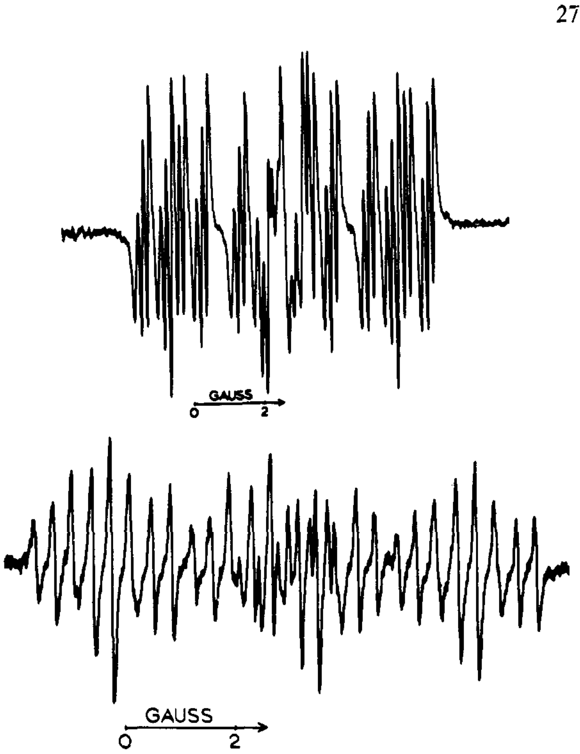


Figure 3. Esr first-derivative spectra of the potassium salts of **1j** and **1k**: top, N-hydroxyisatinsemidione dianion in dimethyl sulfoxide solution; bottom, N-hydroxyisatinsemidione in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) solution.

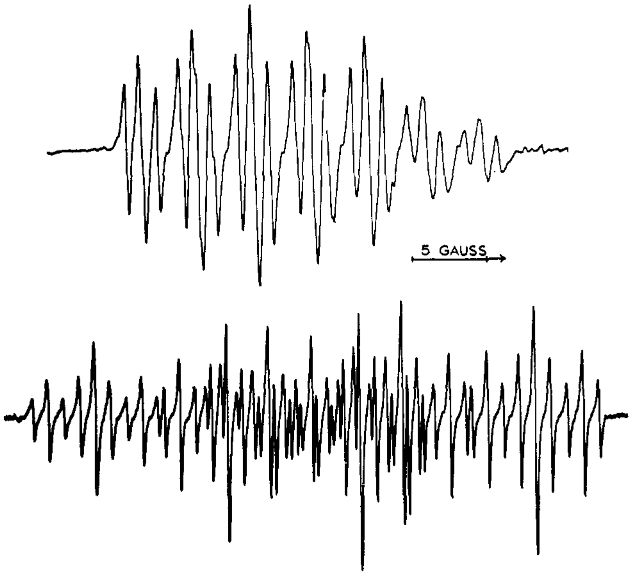


Figure 4. Esr first-derivative spectra of **5a** and **5b** in dimethyl sulfoxide solution: top, *o*-carboxynitrosobenzene radical anion; bottom, *o*-carboxyphenyl nitroxide.

N-Hydroxyisatin can be converted into semidiones **1j** and **1k**. The situation is somewhat complicated since we recognize that 4 other paramagnetic species can be formed from N-hydroxyisatin under the appropriate conditions (see Chart I). N-Hydroxyisatin in DMSO containing excess potassium *t*-butoxide and propiophenone yields the radical dianion **1k** which may also be formed by the oxidation of N-hydroxyoxindole in DMSO solutions containing excess potassium *t*-butoxide. In DMSO (80%)-*t*-butyl alcohol (20%) a spectrum is obtained (Figure 3) from either N-hydroxyisatin or N-hydroxyoxindole that is attributed to the conjugate acid of **1k**, the radical anion **1j**. Treatment of N-hydroxyisatin with potassium *t*-butoxide in hexamethylphosphoramide leads to either the nitroxide **5a** or the nitrosobenzene radical anion **5b** depending upon the concentration of base (Figure 4). The nitroxide radical was also made by the autoxidation of *o*-carboxyphenylhydroxylamine in basic solution or by oxidation of the hydroxylamine with lead dioxide or lead tetraacetate in the absence of base.[17] The ni-

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(17) G. A. Russell, E. J. Geels, F. J. Smentowski, K.-Y. Chang, J. Reynolds, and G. Kaupp, *J. Amer. Chem. Soc.*, **89**, 3821 (1967).

Table IV. Hyperfine Splitting Constants (G) for **5a** and **5b**[a]

Radical	Solvent	Base (M)	a^N	a_{NH}^H	$a_{o,p}^H$	a_m^H
5a	DMSO (80%)- *t*-BuOH (20%)	$KOC(CH_3)_3$ (0.1)	8.85	11.62	3.20	1.02
5a	CH_3OH (25%)- H_2O (75%)	NaOH (0.3)	10.00	12.80	3.50	1.13
5a	DMSO		8.70	11.80	3.13	1.00
5a	Pyridine		8.50	11.65	3.05	1.00
5a	Dioxane		8.10	11.75	3.00	1.00
5b	DMSO	$KOC(CH_3)_3$ (1)	7.65		3.90, 3.68	1.16, 1.08
5b	DMSO (80%)- *t*-BuOH (20%)	$KOC(CH_3)_3$ (1)	8.20		3.95, 3.68	1.16, 1.02
5b	DMSO (50%)- *t*-BuOH (50%)	$KOC(CH_3)_3$ (1)	8.70		4.00	1.20

[a] *o*, *m*, *p* refer to the nitroso or nitroxide group.

troxide shows typical effects of solvent in hfsc (Table IV). The nitroxide **5a** is recognized to be the product of the electrolytic reduction of *o*-nitrobenzoic acid in DMF-ethanol solution.[18-20]

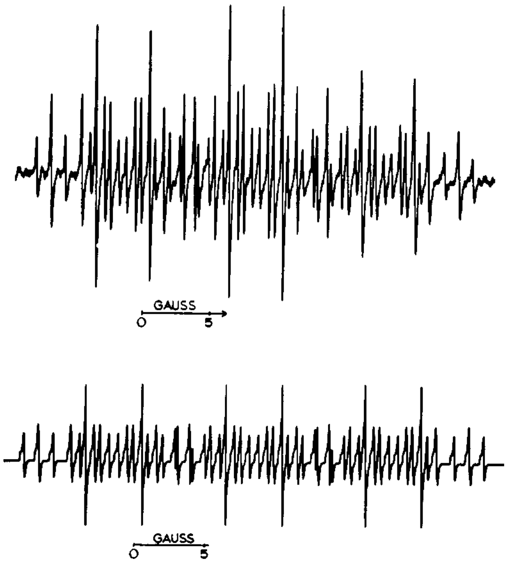


Figure 5. Esr first-derivative spectrum of the potassium salt of **4b** in dimethyl sulfoxide solution: top, observed spectrum; bottom, calculated spectrum with Lorentzian line width of 0.15 G.

A nitroxide to which we assign structure **4b** was formed from N-hydroxyisatin in DMSO or DMF solutions containing potassium *t*-butoxide and in the presence of air (Figure 5). The radical was stable to oxygen but was readily destroyed by the addition of small amounts of water or *t*-butyl alcohol. The stability of **4b** and **1j** to both reagents is in marked contrast. The nitroxide (Figure 5) had a reasonable a^N of 9.85 G and proton splittings of 3.98, 3.35, 3.35, 1.05, and 1.05 G. In DMSO-d_6 solution one of 3.35 G splittings was replaced by $a^D = 0.52$ G.

The assignment of structure **4b** is based on the elimination of structures **4a**, **4c**–**4e** as possibilities. The value of a^N in the nitroxide (9.85 G) excludes a phenyl nitroxide with a carbonyl or a vinyl group adjacent to the nitroxide function.

Nitroxides **3a**–**3c** were prepared by the oxidation of N-hydroxyisatin, N-hydroxydioxindole, and N-hydroxyoxindole by *p*-nitroperbenzoic acid or lead dioxide in dioxane (nitroxides **3** are quite unstable in DMSO solution) (Figure 6). The observed values of a^N for **3a**–**3c** (Table V) seem quite consistent with the value of 7.55 G reported for **8**[21] and excludes structures with a carbonyl group conjugated with the nitroxide function. Moreover, the value of a^H for the benzylic

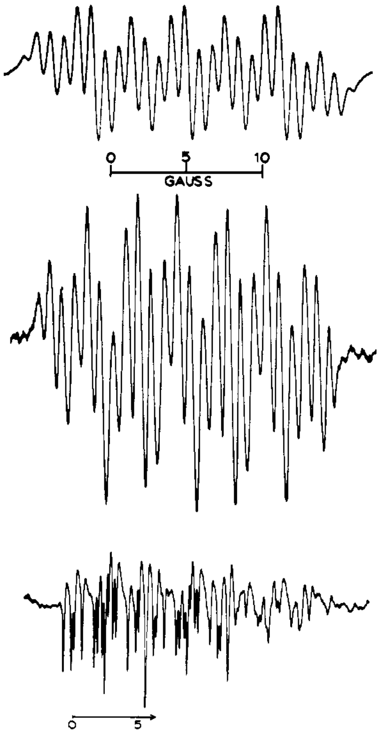
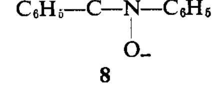


Figure 6. Esr spectra of the nitroxides **3a**, **3b**, and **3c** in dimethyl sulfoxide solution: top, N-hydroxyoxindole nitroxide; middle, N-hydroxydioxindole nitroxide; bottom, spectrum attributed to N-hydroxyisatin nitroxide.



$$C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle O^-}{\underset{|}{\overset{\cdot\,+}{N}}}-C_6H_5$$

8

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(18) P. L. Nordio, M. V. Pavan, and C. Coryaja, *Trans. Faraday Soc.*, 60, 1895 (1964).

(19) P. Ludwig, T. Layoff, and R. N. Adams, *J. Amer. Chem. Soc.*, 86, 4568 (1964).

(20) G. Chapelet-Letourneux, H. Lemaire, A. Rassat, and J.-P. Ravat, *Bull. Soc. Chim. Fr.*, 1975 (1965).

(21) H. G. Aurich and F. Baer, *Tetrahedron Lett.*, 3879 (1965).

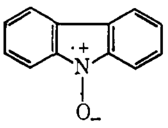
hydrogen atom in **3b** and **3c** clearly excludes **4a** as the structure of the nitroxide obtained from N-hydroxyisatin in basic solution which has a $a_{\text{exchangeable}}^{\text{H}}$ = 3.35 G.

Table V. Hyperfine Splitting Constants (G) for **3** in Dioxane Solution

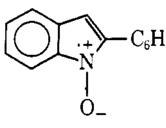
Nitroxide	a^{N}	$a_{\text{benzylic}}^{\text{H}}$	$a_{\text{aromatic}}^{\text{H}}$
3a[a]	6.23		2.56, 2.32, 0.80, 0.59
3b	5.85	0.75	2.50, 2.50, 0.87, 0.87
3c	5.87	0.81, 0.81	2.50, 2.50, 0.87, 0.87

[a] In dimethyl sulfoxide solution.

Structures **4c**, **4d**, and **4e** were eliminated on the basis of a^{N} to be expected in a pyrrole nitroxide. Thus,

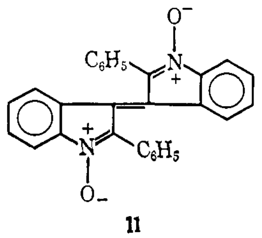


9



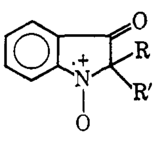
10

9 has a value of a^{N} of 5.4 G,[22] while radical **7** has a^{N} = 5.9 G in DMSO.[23] We have attempted to prepare **10** by the oxidation of N-hydroxy-2-phenylindole. However, oxidation of N-hydroxy-2-phenylindole with lead dioxide in dioxane, methylene chloride, or DMSO yielded **7** with a = 5.56, 6.00, and 5.88; $a^{\text{H}}(2\text{ H})$ = 1.62, 1.62, and 1.62 G, respectively. Radical **7** was also formed when N-hydroxy-2-phenylindole was oxidized with diethyl azoformate. Radical **7** appears to always accompany 1,1′-dioxy-2,2′-diphenyl-$\Delta^{3,3'}$-bi-3*H*-indole (**11**) as an impurity.[9]



11

The value of a^{N} observed for the nitroxide (9.85 G) is thus not consistent with an indole nitroxide structure,[24] but is consistent with structure **4b** (for example, a^{N} is 10 G in **12**).[22]

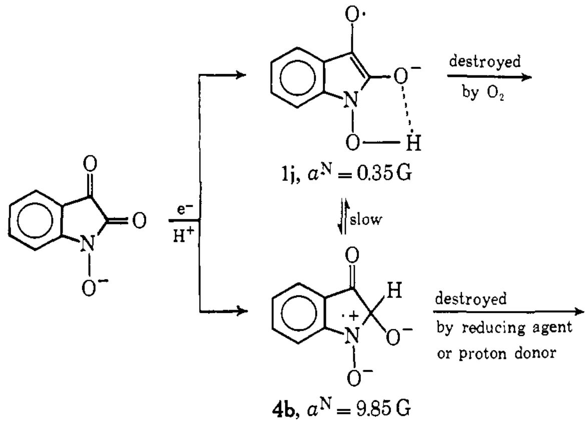


12

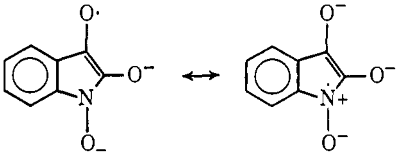
The value of a^{H} exchangeable in **4b** (3.35 G) is much lower than a^{H} in $C_6H_5\overset{\cdot +}{N}(O^-)CH_3$ ($a_{\text{CH}_3}^{\text{H}}$ = 10.4 G).[22] The dihedral angle involved in **4b** is actually better for conjugation (θ = 30°) than in the methyl nitroxide ($\langle\cos^2\theta\rangle = 0.5$). However in **4b** we have a situation in which the spin densities at the nitrogen atom and at C-3 are of opposite sign and partial cancellation occurs. The situation is somewhat analogous to **1a** discussed previously.

The independent existence of the nitroxide **4b** and the isomeric semidione **1j** is surprising. Actually the observation of esr signals due to either **1j** or **4b** may be the result of a kinetic situation. It is readily imaginable that N-hydroxyisatin can be reduced to both **1j** and **4b** in basic solution. Provided that the interconversion of the isomers is slow, it is reasonable that under oxidizing conditions **1j** is destroyed while in the presence of a reducing agent (*e.g.*, propiophenone) or a proton donor **4b** is destroyed. The conditions under which **1j** or **4b** are observed may involve the conversion of N-hydroxyisatin to a mixture of **1j** and **4b**, followed by a preferential scavenging of one of the isomers (Scheme I).

Scheme I



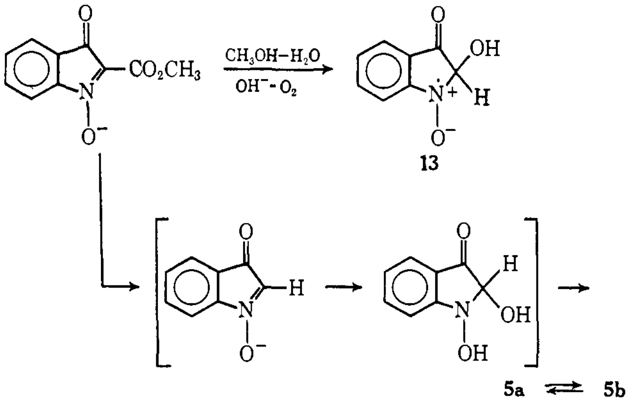
Radical dianion **1k** can be considered to be either a semidione or a nitroxide. The value of a^{N} is certainly in much better agreement with the semidione resonance structure (for example, a^{N} = 0.35 G for **1j**) than the nitroxide structure (a^{N} = 9.85 G for **4b**).



1k, $a^{\text{N}} = 0.17\text{G}$

The identification of **5a** and **5b** is of some interest. A nitroxide prepared from 2-carbomethoxyisatogen

Scheme II



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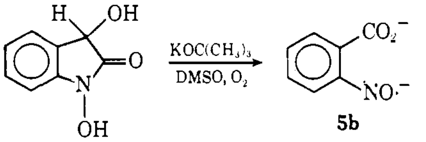
[22] G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull' Soc. Chim. Fr.*, 3283 (1965).

[23] The hfsc are given in ref 9 as a^{N} = 5.80, a^{H} = 0.75 G (2 H). The value of a^{H} is apparently in error by a factor of 2 and should be 1.50 G.

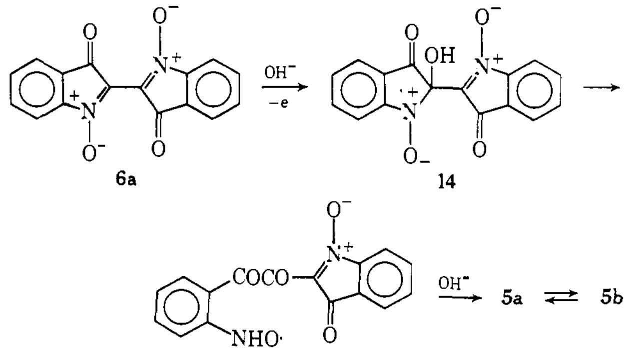
[24] Professor A. Rassat and Dr. R. Ramasseul on the basis of experimental and theoretical work have concluded that a^{N} of a pyrrole nitroxide cannot exceed 7 G (private communication from Dr. R. Ramasseul, July 1969).

had been previously assigned the structure **13** ($a^N = 9.66$, $a^H = 12.48, 3.38, 3.38, 1.08, 1.08$ G).[7] The formulation of this product as the ring-opened nitroxide seems more reasonable (Scheme II). In this regard we have observed that N-hydroxydioxindole when treated with an excess of potassium *t*-butoxide in DMSO solution in the presence of a trace of oxygen also yields **5b**. We also found that the diisatogen **6a** can be



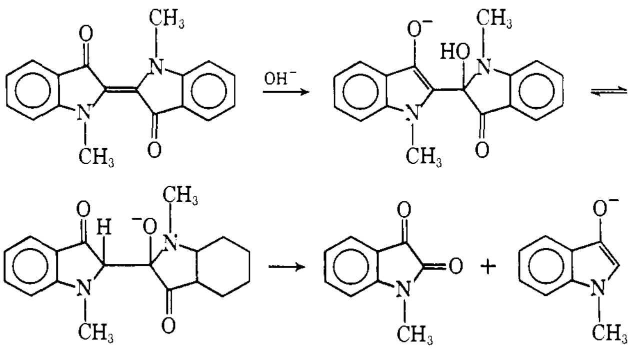
converted to 5a or **5b** in DMSO (80%)-*t*-butyl alcohol (20%) containing an excess of potassium *t*-butoxide, perhaps by the process in Scheme III.

Scheme III

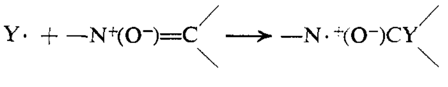


In a similar fashion N,N′-dimethylindigo in DMSO solution proved to be one of the best sources of the N-methylisatin radical anion (Scheme IV). The spectrum of N-methylisatin radical anion was also produced from monomethylindigo in basic solution in the presence of oxygen. However, the yield is much lower than for the dimethyl derivative. All attempts to produce isatin radical anion from indigo itself or from isoindigo in basic solution yielded the indigo or isoindigo radical anions.[25,26] In basic methanol solution indigo is readily reduced to the indigo radical anion by hydrazobenzene.[25] However, under similar conditions N,N′-dimethylindigo yielded only the N-methylisatin radical ion. The presence of hydrazobenzene greatly increased the concentration of the radical anion, presumably by reduction of the N-methylisatin formed by hydrolysis.

Scheme IV



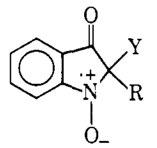
Several nitroxide radicals of unknown structure were detected in this work. They are apparently formed by the addition of a radical to the nitrone grouping[27] of the isatogen. The diisatogen **6a** upon boiling in



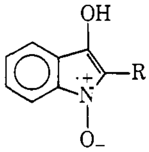
$$\mathrm{Y}\cdot + -\mathrm{N}^{+}(\mathrm{O}^{-})=\mathrm{C}\langle \longrightarrow -\mathrm{N}\cdot^{+}(\mathrm{O}^{-})\mathrm{CY}\langle$$

mesitylene or upon treatment with DMSO (60%)-*t*-butyl alcohol (40%) containing propiophenone and 2 equiv of potassium *t*-butoxide for each mole of the isatogen yielded a radical, $a^N = 9.44$, $a^H = 2.85, 2.85, 1.00, 1.00$ G. Structure **14** seems reasonable and provides a convenient intermediate for the conversion of **6a** to 5a ⇄ **5b**.

Treatment of N-hydroxy-2-phenylindole with lead tetraacetate in the absence of air,[28] or by *p*-nitroperbenzoic acid in dioxane solution, gives a radical with $a^N = 9.50$, $a^H = 3.05, 3.05, 1.00$, and 1.00 G. Structure **15a** seems reasonable where Y may be hydroxyl. Lunazzi, *et al.*, report that 2-phenylisatogen upon photolysis in mesitylene yields a radical with $a^N = 9.24$, $a^H = 2.97, 2.97, 1.05, 1.05, 0.48$ G.[7] Structure **16a** was assigned. We feel that structure **15a** is more reasonable (Y = OH) and that the hydroxyl hydrogen can be resolved in mesitylene more readily than in DMSO solution. Photolysis of 2-carbomethoxyisatogen in acetic acid yielded a radical with $a^N = 9.25$, $a^H = 2.94, 2.94, 0.99, 0.99$ G, which upon dilution with carbon tetrachloride allowed the resolution of another hydrogen, $a^H = 0.5$ G.[7] Again, it appears that **15b**, Y = OH, is a more reasonable structure than the indole nitroxide derivatives **16b**. Moreover, **15b** is a convenient intermediate (Scheme V) for the formation of 5a ⇄ **5b** concerning which we have commented previously. Structure **15**, *e.g.* with R = CH_3, may be the paramagnetic oxidation product of 2-methylindole with *p*-nitroperbenzoic acid ($a^N = 9.8$ G).[22]

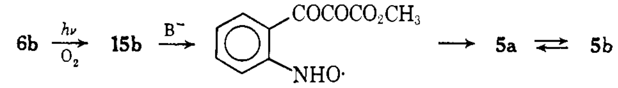


15a, R = C_6H_5
b, R = CO_2CH_3



16a, R = C_6H_5
b, R = CO_2CH_3

Scheme V



Experimental Section

General. The radical ions were prepared by techniques previously described.[16,29] Solutions of a 1,2-diketone, or α-hydroxy ketone, in DMSO or other solvent were placed in one leg of the inverted U cell[16] and deoxygenated by a stream of prepurified nitrogen. Base and solvent in the other leg were simultaneously deoxygenated. After about 15 min of deoxygenation, the solutions

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[25] G. A. Russell and R. Konaka, *J. Org. Chem.*, **32**, 234 (1967); G. A. Russell, R. Konaka, E. T. Strom, W. C. Danen, G. Kaupp, and K.-Y. Chang, *J. Amer. Chem. Soc.*, **90**, 4646 (1968).

[26] G. A. Russell and G. Kaupp, *ibid.*, **91**, 3851 (1969).

[27] E. G. Janzen and B. J. Blackburn, *ibid.*, **90**, 5909 (1968).

[28] It is known that the oxidation of N-hydroxy-2-phenylindole with lead tetraacetate leads to 2-phenylisatogen: M. Colonna and P. Bruni, *Gazz. Chim. Ital.*, **95**, 1187 (1965).

[29] G. A. Russell and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 744 (1964).

were mixed by inverting the cell and the final solution was shaken into Varian V-4548 aqueous solution sample cell. The radical concentration was monitored by a Varian E-3 spectrometer at 30°. Approximately 5 mg of potassium *t*-butoxide and 5 mg of the diketone were used in 5 ml of DMSO. In oxidation experiments the solutions were first deoxygenated and mixed. The cell was then opened at the joint between the aqueous sample cell and the mixing cell for 5–10 sec and air allowed to diffuse into the mixing cell. The solution was then vigorously shaken and the esr spectrum recorded. The process was repeated when further oxidation was required.

The synthesis of nitroxides was performed in the inverted U cell by mixing of a solution of the substrate and lead tetraacetate or *p*-nitrobenzoic acid. For lead dioxide syntheses a solution of the substrate was first deoxygenated in the cell and then powdered lead dioxide added and the solution vigorously shaken. The assignments of hfsc were verified by calculation of the spectra using a Japanese Electron Optics Corp. HNM-RA-1 spectrum accumulator. Lorentzian line widths in the range of 0.10–0.15 G were commonly encountered.

1,2-Indan semidiones. 1,2-Indansemidione was formed by treatment of 1,2-indandione[30] or 2-acetoxy-1-indanone[5] with an equivalent amount of potassium *t*-butoxide in DMSO solution. A 5-fold excess of potassium *t*-butoxide produced a different esr spectrum, $a^{\mathrm{H}} = 4.03, 2.92, 1.58, 1.58, 0.97, 0.97, 0.61, 0.61$ G, probably due to intermolecular condensation. 3,3-Dimethoxy-1,2-indandione[31] also produced a semidione upon treatment with basic DMSO. However, the 2,2-dimethoxy isomer failed to yield an esr signal under these conditions. 3,3-Dimethylindan-1,2-dione was prepared from β-phenylisovaleric acid following the procedure of Koelsch and LeClaire;[32] mp 101–102°, lit.[32] mp 106–107°; mass spectrum (70 eV), molecular ion at *m/e* = 174.

Other Reagents. Coumarin-2,3-dione was synthesized following the procedures of Baeyer[33] and Fries.[34] Isatin (0.1 mol) was dissolved in 150 ml of 1 *N* aqueous sodium hydroxide. Sodium nitrite (7 g) was added and the solution cooled in an ice bath. To the cold solution, 150 ml of 2.5 *M* sulfuric acid was added slowly. The solution was stirred for 10 min and then warmed to 60° and allowed to stand for 1 hr with occasional shaking. The solution was filtered from activated charcoal and extracted with ether. Drying and removal of the solvent left crude 2-hydroxyphenylglyoxylic acid. The entire preparation of acid was dissolved in 300 ml of benzene and 200 ml of heptane. Phosphorus pentoxide (15 g) was added and the mixture refluxed for 30 min. The solution was filtered and evaporated to 50 ml. Addition of hexane produced a yellow solid. Recrystallization from benzene–hexane gave material with mp 128–130°, lit.[35] 132°; mass spectrum (70 eV), molecular ion at *m/e* = 148. 5-Methylisatin was converted into **5-methylcoumaran-2,3-dione** by the above procedure; mp 146°, lit.[35] mp 149°; mass spectrum (70 eV), molecular ion at *m/e* = 162.

Thianaphthenequinone was synthesized from thiaindoxyl following the methods of Pummerer[36] and Friedländer.[37] Thioindoxyl (3.2 g) was added to 65 ml of a warm deoxygenated 10% aqueous sodium hydroxide solution. After dissolution the solution was cooled in an ice bath and 2.6 g of nitrosobenzene in 30 ml of ethanol added dropwise with stirring. The red precipitate of the anil of thianaphthenequinone was collected by filtration (3.2 g, 63%). The anil was refluxed in 100 ml of 33% sulfuric acid for 3 hr. The solution was filtered while hot and the cooled filtrate extracted with chloroform. Evaporation of the solvent left a yellow crystalline solid that was recrystallized from benzene-hexane to give mp 118°, lit.[37] mp 121°; mass spectrum (70 eV), molecular ion at *m/e* = 164. Commercial **isatin** was recrystallized from benzene, mp 200°. **N-Deuterioisatin** was prepared by crystallizing isatin twice from D_2O. The purity was verified by pmr. **5-Methylisatin** was prepared by the method of Marvel[38] anion in DMSO (80%)–*t*-butyl alcohol (20%) by reaction with 5-methyldioxindole; $a^{\mathrm{H}} = 3.67, 3.15, 0.98, 0.19$; $a_{\mathrm{CH_3}}{}^{\mathrm{H}} = 0.98$; $a^{\mathrm{N}} = 0.96$ G. Excess base yielded the dianion radical which had the following hfsc in DMSO, $a^{\mathrm{H}} = 4.18, 3.48, 1.02$; $a_{\mathrm{CH_3}}{}^{\mathrm{H}} = 1.02$; $a^{\mathrm{H}} = 0.47$ G.

Commercial **5,7-dichloroisatin** was recrystallized from ethanol, mp 221–222°. Reaction with 5,7-dichlorodioxindole in basic solution yielded the semidione anion and dianion. In DMSO (80%)–*t*-butyl alcohol (20%) the radical anion had $a^{\mathrm{H}} = 4.0, 3.2$, $a^{\mathrm{N}} = 1.1$ G, and the radical dianion $a^{\mathrm{H}} = 4.4, 3.4$, $a^{\mathrm{N}} = 0.6$ G. **Isatide** was prepared by the condensation of isatin (1.0 g) with dioxindole (1.015 g) in 60 ml of ethanol containing 0.5 g of morpholine. Heating for 1 hr on a steam bath yielded 1.25 g (62.5%) of isatide, mp 225°, lit.[39,40] mp 230–245°. **Dioxindole** was prepared by the reduction of isatin by sodium dithionite in aqueous solution.[41] Recrystallization from water gave material mp 165°, lit.[39] 167–170°; mass spectrum (70 eV), molecular ion at *m/e* 149. 5-Methyldioxindole was prepared by refluxing a solution of 5-methylisatin and sodium dithionite in 50% aqueous ethanol for 15 min, mp 225–240°; mass spectrum (70 eV), molecular ion at *m/e* = 163.

Anal. Calcd for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.66; H, 5.57; N, 8.65.

5,7-Dichlorodioxindole had mp 215–230°. *Anal.* Calcd for $C_8H_5Cl_2NO_2$: C, 44.06; H, 2.31; N, 6.42; Cl, 32.52. Found: C, 44.25; H, 2.30; N, 6.29; Cl, 32.39.

N-Methylisatin was prepared from 15 g of isatin and 36 g of dimethyl sulfate dissolved in 80 ml of 10% aqueous sodium hydroxide. After refluxing for 3 hr the solution was cooled in an ice bath and the solid precipitate collected by filtration. The product was dissolved in chloroform–methanol and eluted from a silica gel column with benzene. Recrystallization from benzene gave material with mp 131°, lit.[42] 134°. Commercial **oxindole** was recrystallized from benzene, mp 127°. **N-Hydroxyoxindole** was prepared from commercial *o*-nitrophenylpyruvic acid;[43] mp 200°, lit.[43] 199–201°. **N-Hydroxydioxindole** was prepared by the reduction of *o*-nitromandelic acid by zinc and aqueous ammonium chloride;[44] mp 172°, lit.[44] 167–172°. **N-Hydroxyisatin** was prepared by the action of acid on *o*-nitrodiazoacetophenone,[45] mp 190–192°, lit.[45] 193°. **1-Hydroxy-2-phenylindole** was prepared according to the direction of Fischer.[46] **2-Phenylisatogen** was prepared by the reaction of molar equivalents of 1-hydroxy-2-phenylindole and *p*-nitrobenzoic acid in ether over a period of 20 days at 25°. A quantitative yield of 2-phenylisatogen was collected by filtration, mp 188°, lit.[47] 187–188°. **Dehydroindigo 1,1′-dioxide** (diisatogen) was prepared from 2,2′-dinitrodiphenyldiacetylene according to the method of Ruggli and Bolliger,[48] mp 287° dec, lit.[48] 287° dec. The preparation of **1,1-dioxy-2,2′-diphenyl-$\Delta^{3,3'}$-bi-3*H*-indole** has been described.[8,49] **2-Carboxyphenylhydroxylamine** was prepared by the reduction of *o*-nitrobenzoic acid with zinc and aqueous ammonium chloride,[50] mp 142°, lit.[50] mp 142.5°. 2-Nitrosobenzoic acid was prepared by the oxidation of 2-carboxyphenylhydroxylamine with ferric chloride,[50] mp 214°, lit.[51] mp 205–210° dec.

Acknowledgment. Dr. Gerd Kaupp prepared the 5-methylisatin, monomethylindigo, and N,N′-dimethylindigo. N-Hydroxyisatin was a gift from Mr. L. J. Darlage and Dr. T. J. Kinstle. 2-Carboxyphenylhydroxylamine was prepared by Dr. T. Metcalfe. Valuable suggestions were provided by Dr. A. Mackor and Dr. R. Ramasseul.

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(41) C. Marschalk, *ibid.*, **45**, 582 (1912).

(42) W. Borsche and W. Jacobs, *ibid.*, **47**, 354 (1914).

(43) W. B. Wright and K. H. Collins, *J. Amer. Chem. Soc.*, **78**, 221 (1956).

(44) G. Heller, *Chem. Ber.*, **42**, 470 (1909).

(45) F. Arndt, B. Eistert, and W. Partate, *ibid.*, **60**, 1364 (1927); E. C. Taylor and D. R. Eckroth, *Tetrahedron*, 20, 2059 (1964).

(46) E. Fischer, *Chem. Ber.*, **28**, 586 (1895); **29**, 2062 (1896).

(47) F. Krohnke, *ibid.*, **84**, 932 (1951); **85**, 376 (1952).

(48) P. Ruggli and A. Bolliger, *Helv. Chim. Acta*, **4**, 626 (1921).

(49) M. Colonna and P. Bruni, *Gazz. Chim. Ital.*, **95**, 1172 (1965).

(50) E. Bamberger and F. L. Pyman, *Chem. Ber.*, **42**, 2297 (1909).

(51) G. Ciamician and P. Silber, *ibid.*, **34**, 2040 (1901).