Heterocyclic Radical Anions. II. Naphthalic and 1,4,5,8-Naphthalenetetracarboxylic Acid Derivatives

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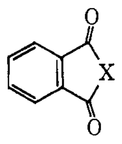
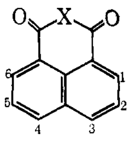
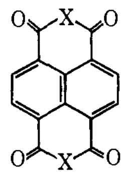
Abstract: The esr spectra of electrolytically generated naphthalic anhydride and naphthalimide anions are discussed. Di-*t*-butyl substitution is used to prove assignments and simplify spectra. At high potentials or in base the unsubstituted imides and 1,3-*peri*-naphthindinedione deprotonate and dianion radicals are observed. At high potentials the anhydrides form species assigned to protonated three-electron reduction products. McLachlan calculations of spin density for the radicals are discussed. Esr evidence for strong conformational preference in the N-ethyl imides and restricted rotation of *t*-butyls in the di-*o*-*t*-butylated anhydride are presented. Conclusions in the 1,4,5,8-naphthalenetetracarboxylic bisimide system are similar. The bisdeprotonated trianion radical was observed from the bisimide.

In part I[1] we considered the esr spectra of anions of phthalic anhydride, phthalimides, and 1,3-indandiones, represented as structure I. Here, we shall discuss the spectra of 1,8-naphthalic acid (II) and naphthalene-1,4,5,8-tetracarboxylic acid derivatives (III). For II and III, as for I, the odd-electron MO of the anion has by symmetry a node through the X group, but Hückel theory is expected to be inadequate, since electron correlation will result in significant spin at the X group. The parent hydrocarbon radicals of II and III (without the oxygens), *peri*-naphthenyl,[2] and pyrene anion[3] were among the first alternate hydrocarbons for which significant deviations from HMO spin densities were observed. Correlation of esr-derived spin densities with McLachlan calculations would show how well this simple SCF approximation will predict the spin densities, and also allow choice of the best *h* and *k* parameters[4] for the various carbonyl–X group combinations studied. These spectra also afford further examples[1] of N–H and N-alkyl splittings in anions, which should help to establish *Q* values for such splittings. In order to simplify the spectra (for II, $X = N\text{-}CH_3$, there are 324 lines, which results in poorly resolved spectra), we have employed *t*-butyl substitution at positions 2 and 5 (IIA). The π system is only slightly perturbed by such substitution, and the H_2,H_5 triplet is effectively eliminated from the spectrum. This results in significant simplification for the imide spectra, since the alkyl splittings are close to those of H_2 and H_5. We found that 1,6-di-*t*-butylnaphthalic anhydride (IIB, X = O) shows a line width of over 0.5 gauss; the spin density of the 1,6-positions is so high that significant splitting by the *t*-butyl hydrogen is observed.


I



II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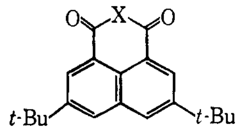
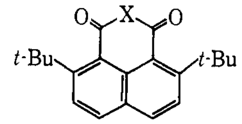

IIA


IIB

Experimental Section

Commercial naphthalic anhydride and naphthalimide were crystallized from methyl benzoate. 2,5-Di-*t*-butylnaphthalic anhydride,[5] its unsubstituted[6] (mp 239–240.5°, lit.[6] 240°), N-methyl[6] (mp 234–235.5°, lit.[6] 231–232°), and N-ethyl imides (mp 242–244°), 1,3-*peri*-naphthindanedione,[7] naphthalide,[8] and naphthaldehydic acid[9] were prepared by standard methods.

1,6-Di-*t*-butylnaphthalic Anhydride (IIB, X = O). As Illingworth and Peters have observed,[10] oxidation of 1,6-di-*t*-butylacenaphthene with sodium dichromate in acetic acid, even for extended periods, only affords a yellow mixture of quinone and anhydride which is inseparable by ordinary techniques.[10] The mixture (mp 123–127°, lit.[10] 127–131°) was conveniently analyzed by polarography, as one-electron waves for reduction for quinone and anhydride are observed at −0.86 and −1.17 v (*vs.* sce, in DMSO); our mixture was 20:80 from the height ratio. White, crystalline anhydride (mp 133–135°) was obtained by adding 30 mg of ceric ammonium nitrate to the mixture (1 g) and sodium dichromate (3.5 g), and refluxing 12 hr in acetic acid. No quinone was detected by esr or polarography. The nmr spectrum (DMSO, 60 Mc) showed a singlet (half-width = 1.0 Hz) at δ 1.59 (18 H), and an AB quartet (4 H at δ 8.05 and 8.36, J = 8.8 Hz). The ultraviolet spectrum (chloroform) had maxima at 340 mμ (ϵ 1.2×10^4) and 349 (1.3×10^4); comparison with the 2,5-di-*t*-butyl isomer, which has maxima at 338 (1.33×10^4) and 351 (1.59×10^4), gives no evidence for the considerable strain of the *t*-butyl groups forcing nonplanarity.

The **1,4,5,8-naphthalenetetracarboxylic** bisimides were prepared by boiling the bisanhydride in excess aqueous amine. Only the ethyl bisimide was soluble enough for recrystallization (methyl benzoate). The others were used crude; "clean" esr spectra and polarograms demonstrated any impurities were not easily reducible. None melted below 300°.

A Varian 100-kc V-4502 spectrometer with 9-in. magnet was employed. "Fieldial" calibration periodically checked using Fremy's salt was used to measure splitting constants. Electrolyses

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(1) S. F. Nelsen, *J. Am. Chem. Soc.*, **89**, 5256 (1967).

(2) P. B. Sogo, M. Nakazaki, and M. Calvin, *J. Chem. Phys.*, **26**, 1343 (1957).

(3) G. J. Hoijtink, J. Townsend, and S. I. Weissman, *ibid.*, **34**, 507 (1961).

(4) A. Streitwiesser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 5.

(5) K. E. Nursten and A. T. Peters, *J. Chem. Soc.*, 729 (1950).

(6) A. T. Peters, *ibid.*, 562 (1942).

(7) G. Erreva, *Gazz. Chim. Ital.*, **4**, 190 (1911); see *Chem. Zentr.*, 1633 (1911).

(8) J. Cason and J. Wordie, *J. Org. Chem.*, **15**, 608 (1950).

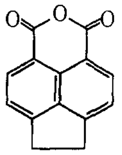
(9) R. C. Fuson and G. Munn, *J. Am. Chem. Soc.*, **71**, 1870 (1949).

(10) E. Illingworth and A. T. Peters, *J. Chem. Soc.*, 1602 (1951).

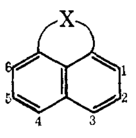
were conducted *in situ* in the Varian flat cell, using DMSO (stored over calcium hydride) which was 0.1 *M* in tetraethyl- or tetrabutylammonium perchlorate as solvents. The splitting constants reported should be accurate to ±0.02 gauss. A Sargent XV polarograph with a Model "A" infrared compensator was employed, the sce reference electrode being isolated from the nonaqueous solution by a closed ungreased stopcock. Half-wave potentials include the liquid junction potential between aqueous and nonaqueous solutions.

Results

To determine the effect of *t*-butyl substitution on the ring splittings, spectra of the *t*-butylated acenaphthylenes and quinones[5] were determined, as well as the II derivative. Since the *peri*-(3,4-di-*t*-butyl) system is not available, we used the 3,4-bridged anhydride[11] IV for comparison of alkyl substitution at the *peri* positions with the others. Observed splittings for the acenaphthenes, quinones, anhydrides, and *peri*-naphthylenediones appear as in Table I. For convenience, these compounds are represented as structure V.



IV



V

Pyracene anion (Table I, column 4, entry one) has not been run under our conditions, but acenaphthene gives values very similar to those of Colpa and deBoer,[12] the splittings being only 1.0–2.2% *lower* at each position. Although esr will obviously never replace nmr for structure proof, it is interesting to note that the 2,5- and 1,6-di-*t*-butylacenaphthylenes are conclusively oriented and show splittings expected. Nmr is particularly misleading for the 1,6 isomer, for the 2,5 and 3,5 protons appear anomalously as a 1.5-cps half-width singlet. For symmetrically substituted naphthylene systems (and other aromatic systems where the number of lines is small enough for resolution), esr does have advantages over nmr since very different splitting constants are shown by different isomers. Our results for naphthalic anhydride do not agree with those of Sioda and Koski,[13] who used DMF (0.03 *M* in tetrabutylammonium perchlorate) at room temperature. In DMF (0.1 *M* in tetraethylammonium perchlorate) we obtain spectra similar to theirs (not resolving a difference between a_1–a_2 and a_3), but we observe splittings of 5.07, 0.85, and 5.92 gauss, a factor of 1.40 ± 0.01 greater than they report. A similar discrepancy was found for naphthalimide (see below), our DMSO splittings being 1.36–1.41 times larger than their splittings (in DMF), except for the small NH splitting, where the discrepancy factor is 1.29. Apparently a calibration error occurred.

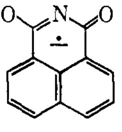
Table I. Splitting Constants (gauss) of Alkylated Acenaphthene Derivative (V) Anions[a]

X		Unsubstituted	2,5-Di-*t*-butyl	1,6-Di-*t*-butyl	3,4-Dimethylene
CH_2–CH_2	a_{CH_2}	7.43 (7.53)[b]	7.58	7.22	(6.58)[b]
	a_1	1.03 (1.04)	0.99	. . .	(1.58)
	a_2	2.38 (2.42)	. . .	2.16	. . .
	a_3	4.08 (4.17)	3.79	4.32	. . .
$-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-$	a_1	1.18[c]		*d*	1.15[c]
	a_2	0.27		0.34	0.21
	a_3	1.28		1.40	. . .
	a_{CH_2}	. . .		. . .	1.38
$-\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}-$	a_1	5.13	5.16	. . .	5.55
	a_2	0.91	. . .	1.26	1.27
	a_3	5.80	5.63	5.99	. . .
	a_{CH_2}	. . .	. . .	. . .	9.19

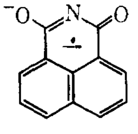
[a] At room temperature in DMSO. [b] I. P. Colpa and E. deBoer, *Mol. Phys.*, **7**, 333 (1963). At −80° in THE, alkali metal reduction. [c] B. M. Trost and S. F. Nelsen, *J. Am. Chem. Soc.*, **88**, 2788 (1966). [d] Line width *ca.* 180 mgauss (peak to peak of derivative curve).

The anion of 2,5-di-*t*-butylnaphthalic anhydride shows the expected nine lines, as does the 1,6 isomer (Figure 1), but in the latter case line widths in excess of 560 mgauss were observed under conditions of ordinary resolution. At higher resolution, fine structure from the *t*-butyl hydrogens could be resolved (Figure 2). The splitting constant for the *t*-butyl groups was *ca.* 0.11 gauss.

The naphthalimide anion spectrum, with 162 lines in 25.9 gauss, was not particularly well resolved, so the N-alkylated imides were studied in the 2,5-di-*t*-butyl series (IIA). As with phthalimide[1] at high potentials with both N–H substituted imides the initial spectrum fades and is replaced by a spectrum not showing splitting by the N–H hydrogen. Only the latter spectrum was obtained when the supporting electrolyte was 10^{-2} *M* in potassium *t*-butoxide. Although these spectra could be considered to be caused by an enol (VIA), the equality observed for 1,6, 2,5, and 3,4-hydrogen splittings, would only occur if equilibration of the two enol forms were rapid compared to $h/g\beta\Delta a$. Rieger and Fraenkel[14] have observed quite different ring splittings in DMF for what is most reasonably the enol form of phthalimide anion. Obtaining the same spectra in base is also a powerful argument. A condensation product would be expected to show splittings from both rings. We therefore prefer the deprotonated dianion structure VIB for these radicals, and write the substituent on nitrogen in the "deprotonated" spectra as ⊖ (an electron pair). The N-alkylated imides showed the expected spectra. Reduction of *peri*-naphthindanedione (II, X = CH_2) at high concentration (10^{-2} *M*) gives a spectrum consisting of a quintet of quartets; the structure of this species is unknown. At lower concentration or in electrolyte



VIA



VIB

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(11) We thank Professor Trost for a sample.
(12) See footnote *b*, Table I.
(13) R. E. Sioda and W. S. Koski, *J. Am. Chem. Soc.*, **89**, 475 (1967).
(14) P. H. Rieger, Ph.D. Thesis, Columbia University, cited by Sioda and Koski.[13]

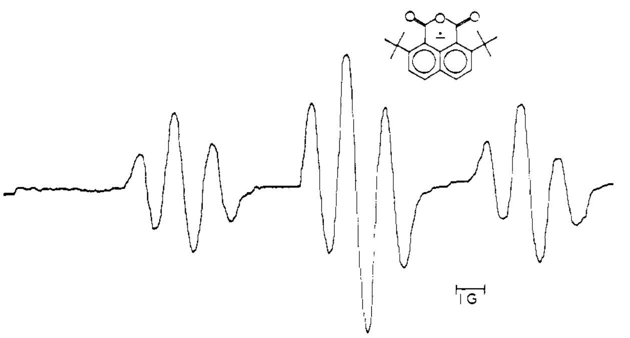


Figure 1. 1,6-Di-*t*-butylnaphthalic anhydride (IIB, X = O) anion at low resolution.

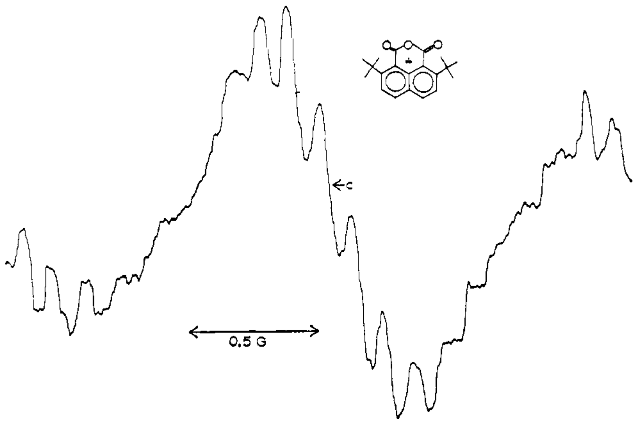


Figure 2. The central line of 1,6-di-*t*-butylnaphthalic anhydride anion at higher resolution.

containing 10^{-2} *M* *t*-butoxide, the spectrum obtained showed three pairs and one single hydrogen (Figure 3). We assign this structure to the deprotonated species analogous to VIB. Observed splitting constants appear as in Table II.

Table II. Esr Splitting Constants of Reduction Products of Naphthalimides and 1,3-*peri*-Naphthindonedione

	II, X = NR		
	R = ⊖	R = H	II, X = $^-$CH
a_1	4.06	4.90	4.14
a_2	0.22	0.79	0.34
a_3	5.51	5.68	5.21
a_N	0.98	1.34	...
a_R	...	0.49 (1 H)	0.75 (1 H)

	2,5-Di-*t*-butyl system (IIA, X = NR)			
	R = ⊖	R = H	R = CH_3	R = CH_2CH_3
a_1	4.08	4.98	4.96	4.98
a_3	4.96	5.47	5.46	5.43
a_N	1.01	1.39	1.49	1.46
a_R	...	0.48 (1 H)	0.63 (3 H)	0.37 (2 H)

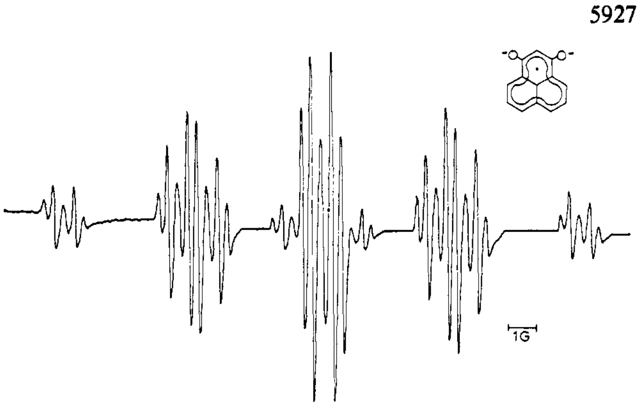


Figure 3. Deprotonated *peri*-naphthindanedione (II, X = CH$^-$) anion obtained in 10^{-2} *M* *t*-butoxide.

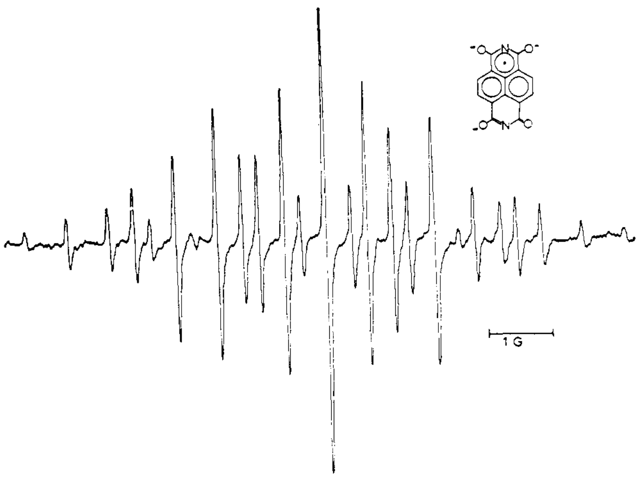


Figure 4. Bisdeprotonated 1,4,5,8-naphthalenetetracarboxylic bisimide anion (III, X = N$^-$), obtained from the bisimide at high applied potential.

Anhydrides and imides in the 1,4,5,8-naphthalenetetracarboxylic acid system showed quite similar behavior. The anhydride anion is remarkably stable; addition of 5% water to the DMSO solution did not cause extensive decomposition. The initial anion radical spectrum from the bisimide fades at high applied potential to give a 25-line pattern (Figure 4) after passing through a transient species we assume to be the monodeprotonated radical. We assign the 25-line pattern (1:2:3:2:1 quintet superimposed on a 1:4:6:4:1 quintet with larger splitting constant) to the bisdeprotonated trianion radical, and once again, in 0.01 *M* *t*-butoxide only this species was observed. For both anion and trianion radical 50–70-mg peak-to-peak line widths were attained, as narrow as any in this group of radicals. A line width of 60 mgauss was also observed for the bisethylimide, although a difference between $2a_N$ and a_H could not be resolved; these quantities must be identical to within 0.01 gauss. The same equality was found for the bismethyl imide, but more lines reresulted in greater accidental overlap. Table III contains the splitting constants observed.

Table III. Esr Splittings for 1,4,5,8-Naphthalenetetracarboxylic Acid Derivatives (III)

X	a_1	a_N	a_R
O	2.00	...	...
N$^-$	1.72_7	0.66_7	...
NH	1.94_2	0.89_4	0.18_6 (1 H)
NCH_3	1.90	0.95	0.39 (3 H)
NCH_2CH_3	1.90	0.95	0.21_7 (2 H)

At high applied potentials all of the initial anion spectra fade due to reduction to diamagnetic species (although deprotonation may occur first).

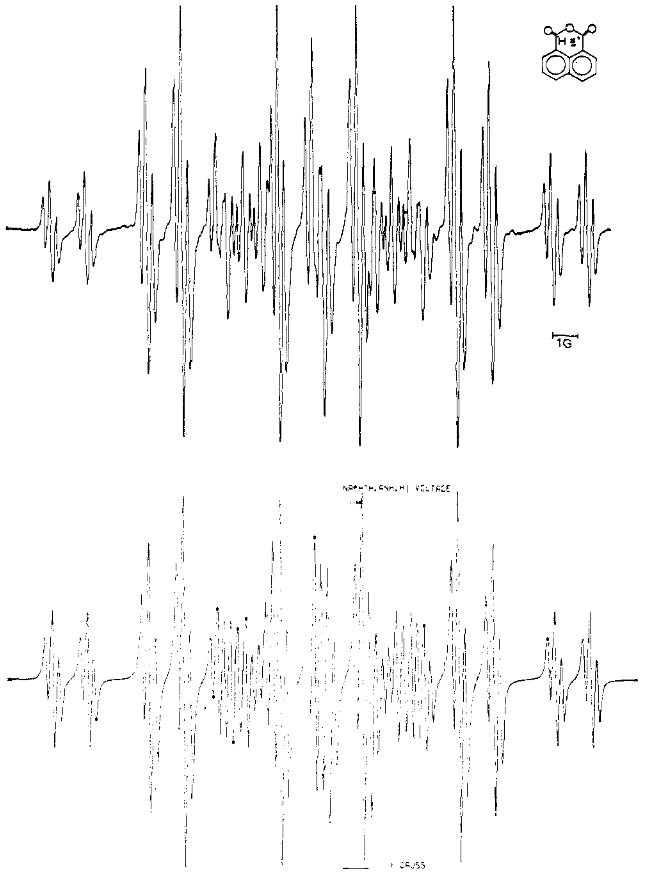


Figure 5. Secondary species from naphthalic anhydride at high potential. The lower curve is a spectrum calculated with the splittings of Table IV, and a line width of 0.10 gauss.

For the naphthalic anhydrides and none of the other compounds studied, "secondary" spectra showing one more proton splitting than starting material appear. Splitting constants for the three naphthalic anhydrides studied appear as in Table IV (we were not able to obtain a "secondary" spectrum from V).

Table IV. "Secondary" Esr Spectra from Naphthalic Anhydrides (Each Splitting Is Written Separately)

II (X = O) Unsubstituted	IIA (X = O) 2,5-Di-*t*-butyl	IIB (X = O) 1,6-Di-*t*-butyl[a]
7.09	7.04	*Ca.* 7.13
5.19	5.12	
3.82	3.78	*Ca.* 1.88
3.82	3.78	*Ca.* 1.88
1.39		*Ca.* 1.88
0.27	0.26	
0.27		(?)

[a] Line width was 350 mgauss, which would have obscured the other expected splitting of 0.3 gauss.

Although the unsubstituted anhydride (Figure 5) showed two pairs of equivalent splittings, the 2,5-di-*t*-butyl anhydride spectrum (Figure 6) makes it clear that equality is accidental, for the 1.39- and one 0.27-gauss splitting in II (X = O) were caused by the 2 and 5 ring protons. The large line widths caused by high spin density at C_1 and/or C_6 for the 1,6-di-*t*-butyl anhydride make interpretation less than sure. We observed two broad 1:3:3:1 quartets, but a small splitting would not have been observed. The "new" proton must be bound to carbon, for OH hydrogens would exchange too fast to show splittings under our conditions. Since higher potential is definitely necessary to form the species giving rise to the secondary spectra, most reasonably a further reduction product of the anhydride has been formed. The spectra are not of condensation products since splittings by only one naphthalene ring are present. Carbonyl reduction was a likely possibility but naphthaldehydic acid (VII), which exists primarily as the hydroxy lactone in DMSO, gives a completely different spectrum (as do the less likely possibilities of naphthalide and naphthoic acid).

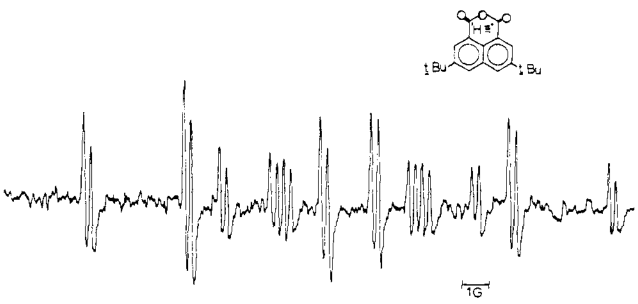
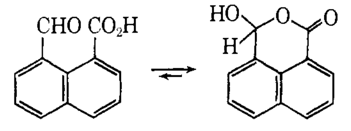
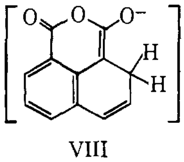


Figure 6. The secondary radical from 2,5-di-*t*-butylnaphthalic anhydride (IIA, X = O) at high potential. Decomposition during the scan is obvious.

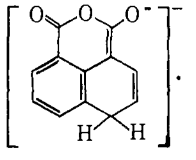


VIIa VIIb

We suggest that present data are most economically explained by ring protonation (preceded or followed by further reduction) to VIII or IX (see Discussion).



VIII



IX

The difference in electrochemical behavior of naphthalic imides and anhydrides is obvious from the polarographic reduction curves. The imides show two waves of close to equal height corresponding to one electron reduction to anion radical and diamagnetic dianion while the anhydrides show one or two overlapping waves about 20–30% of the height of the first wave in the region where the second wave is expected. 1,3-*peri*-Naphthindanedione does not show clear waves at all, but inflections at *ca.* 0.91 and 1.89 v *vs.* sce, and smeared out increase in between. This behavior could be expected for reduction of enol and keto forms in equilibrium in solution. Polarographic results for the compounds studied are summarized in Table V. Although polarographic reduction of the anhydrides results in less than one electron being taken up at the second wave(s) this does not preclude our "secondary" radicals being three-electron reduction products. Polarography only gives information about processe

Table V. Polarographic Data, DMSO 0.1 *M* in Tetraethylammonium Perchlorate; Supporting Electrolyte Voltages Are *vs.* sce (±0.02)

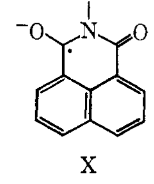
Compd	First wave	Second wave	Height ratio (first/second)
II (X = O)[a]	−1.08	−1.61, −1.70	*Ca.* 3
IIA (X = O)[a]	−1.14	−1.73, −1.81	*Ca.* 3.6–4.6
IIB (X = O)[a]	−1.17	−1.75	*Ca.* 3.0–5.0
IIA (X = NH)	−1.31	−1.96	1.30
IIA (X = NCH_3)[a]	−1.25	−2.02	1.02
IIA (X = NCH_2CH_3)	−1.30	−2.03	1.30
III (X = O)	−0.29	−0.63	0.97
III (X = NH)	−0.48	−0.89	0.99
III (X = NCH_3)	−0.45	−0.91	0.95
III (X = NCH_2CH_3)	−0.46	−0.91	1.02

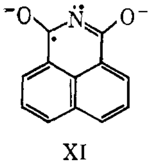
[a] These measurements were performed by Professor D. H. Evans, and are to an accuracy of ±0.01 v.

which are rapid compared to drop lifetime. Several seconds to minutes are required to generate the "secondary" radicals from the anhydrides. The secondary species appear to be formed only under conditions where solvent breakdown is also occurring. Even at the first wave the electrochemistry is unclear. Large-scale electrolysis[15] of IIA (X = O) at 1.5 v *vs.* sce results in more than one electron per molecule being consumed at room temperature, and the current–time plot only approaches a one-electron process at 0° (in acetonitrile). We have been unable as yet to isolate products from electrolysis to allow more conclusive identification of the species giving rise to the secondary spectra.

Discussion

MO Calculations. The spectra of both the II and III systems studied fall into two rather distinct classes. The anhydrides and imides ("L" class) have larger aromatic splittings (a_1 = 4.9–5.2, a_2 = 0.8–1.3, a_3 = 5.4–6.0, a_N = 1.3–1.5) than the deprotonated compounds ("S" class) (a_1 = 4.06–4.2, a_2 = 0.2–0.35, a_3 = 5.0–5.5, a_N = 1.0). There is an obvious shift of spin density out of the ring and away from "X" in the "S" class. The effect is also reflected in the higher *g* factors for the deprotonated imides ($\Delta g \cong 0.0007$) showing greater spin density at oxygen (and hence less at other positions). Valence bond structures such as X and XI exemplify the most important difference between compounds showing the two types of splittings. One might predict from consideration of X and XI that larger k_{CX} and lower k_{CO} values would be necessary for the S class than the L class.


X


XI

We have performed MO calculations on the II system, using h_O values of 0.8, 1.0, 1.3, and 1.6, varying k_{C^*O}, $k_{C'C^*}$ from 1.0 to 1.2, and using auxilliary inductive parameters of $h_{C'}$ = −0.2 to +0.2 and k_{C^*} = −0.2 to +0.2 to find "best" parameters to fit the aromatic splittings ($\alpha_Y = \alpha_C + h_Y\beta_{CC}$, $\beta_{CY} = k_{CY}\beta_{CC}$). Hückel calculations are, as expected, of little utility. Even in McLachlan calculations (λ = 1.2 throughout) the aromatic splittings are extremely insensitive to h_X and k_{C^*X} variation (spin density varies less than ±0.001 for k_{C^*X} = 0.8–1.6 and k_X = 0.0–2.0); practically speaking, the aromatic splittings are independent of these parameters. Choosing $Q^H{}_{CH}$ = 24.0 (McLachlan used 24.2; 23.7 has been used by Fraenkel's group[16]) to obtain experimental spin densities, we obtain about equally good fit for various h_O, k_{C^*O}, and $k_{C'C^*}$ values, for L spectra, as shown in Table VI. Use of auxilliary inductive parameters does not substantially improve the fit. Parameter values which give reasonable fit for ρ_1 and ρ_3 calculated the small and negative ρ_2 too high. Similar behavior was noted by Dehl and Fraenkel[16] for acenaphthoquinone, although in this system better fit is possible. The ρ_1/ρ_3 and ρ_2/ρ_3 ratios may be fit simultaneously by employing a very large auxilliary inductive parameter,[13] but then all the spin densities are 1.4 times too low (see Results). We note that quite different k_{C^*O}/h_O ratios are needed to get reasonable fit in the phthalic[1] and naphthalic anhydride systems, which precludes finding "best" anhydride or imide parameters which will work in any system.

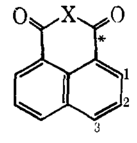

II

Table VI. Comparison of Experimental[a] and Calculated[b] Spin Densities for Naphthalic Anhydride Anion

	Exptl	h_O = 0.8 k_{C^*O} = 1.0 $k_{C'C^*}$ = 1.2	h_O = 1.0 k_{C^*O} = 0.93 $k_{C'C^*}$ = 1.1	h_O = 1.3 k_{C^*O} = 1.15 $k_{C'C^*}$ = 1.1	h_O = 1.6 k_{C^*O} = 1.3 $k_{C'C^*}$ = 1.1
ρ_1	0.214	0.209	0.214	0.212	0.213
ρ_2	0.038	−0.055	−0.059	−0.059	−0.056
ρ_3	0.242	0.246	0.243	0.249	0.252

[a] Calculated using $|Q|$ = 24.0. [b] McLachlan calculation, λ = 1.2.

To fit S-type spectra, position 3 is the most difficult. For any h_O value, increasing k_{CO} lowers ρ_1 and raises (to a less negative value) ρ_2 as needed, but ρ_3 changes much less rapidly. Decreasing $k_{C'C^*}$, increasing h_{C^*}, and decreasing h_C all lower ρ_3. Since there is little reason to expect $k_{C'C^*}$ to be less than 1.0 (indeed, values near 1.2 are needed for planar semidiones[16]) we have employed h_O = 1.3, $k_{C'C^*}$ = 1.0 and varied k_{C^*O}, h_{C^*}, and $h_{C'}$ to find what values are necessary. Results of the calculations appear in Table VII.

We can see little rationalization for the relative values of best fit McLachan parameters for the L and S class spectra; they are more or less opposite to what we intuitively expect. As before, fit to the 2, 5, X negative spin positions is poor if parameters are adjusted to fit the large spin positions; McLachlan theory is not accurate enough.

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(15) Undertaken in collaboration with Professor D. H. Evans.

(16) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

Table VII. MO Calculations of Spin Densities for II (X = $^{-}$CH) Anion Radical

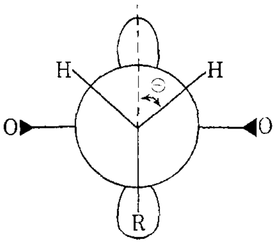
Position	Exptl[a]	Calcd[b]
1	0.166	0.164
2	0.014	−0.040
3	0.208	0.210
X	0.030	−0.064

[a] $Q = 24.0$. [b] $h_O = 1.3$, $k_{C*O} = 1.3$, $k_{C'C*} = 1.0$, $h_{C'} = -0.25$, $h_{C*} = 0.1\ h_O$.

We shall defer discussion of spin densities at oxygen and "X" in these systems until accurate *g* factors are available.

Effect of *t*-Butyl Substitution. Tables I and II demonstrate that 2,5-*t*-butyl substitution in the naphthalene ring lowers a_1 and a_3 slightly (a_1 of the imides is 0.08 gauss larger in the 2,5-dibutyl case, however), whereas 1,6 substitution raises a_3. The effect on a_2 is less regular, significant lowering being observed for the acenaphthene, but raising for the quinone and anhydride. Positional assignments of the splittings are confirmed by the *t*-butylated compounds. The shifts are consistent with the slightly electron-releasing character of alkyl *vs.* hydrogen groups. The 0.11-gauss *t*-butyl splittings of IIB (X = O) are unusually high, comparable to the 0.107-gauss splittings observed using nmr for di-*t*-butyl nitroxide,[17] where ρ_N is probably about one-half. The *ortho* splitting of 2,4,6-tri-*t*-butylphenoxyl is 72 mgauss.[1] Spin density is probably about 0.255 at the *ortho* carbon.[18] IIB (X = O) has an estimated spin density of *ca.* 0.215 at the substituted carbon. Corey–Pauling models show the *t*-butyls of the phenoxide can rotate, but those of the naphthalic anhydride appear surely frozen. If the spin density reaching the *t*-butyl hydrogens depends on C–C hyperconjugation,[19] similar angle dependence of $Q^{H}{}_{C(CH_3)_3}$ to Q_β would be expected (see below for discussion of Q_β). For rotating groups $\langle\cos^2\theta\rangle = 0.50$, but for IIB (X = O) this quantity is 0.75 for two methyls and zero for the third of each *t*-butyl. This leads to a predicted *a*(*t*-butyl) of 90 mgauss (12 H) for IIB (X = O), at least qualitatively explaining the larger a_H with smaller spin density.

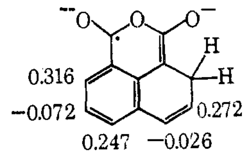
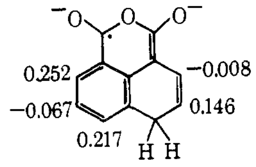
Alkyl Imide Splittings. The ratio of methyl to ethyl methylene splittings in methyl- and ethylphthalimide anions was found to be 1.60 previously.[1] Here we found ratios of 1.70 and 1.77 for similarly substituted 2,5-di-*t*-butylnaphthalimides and 1,4,5,8-naphthalenetetracarboxylic acid bisimides. In no case was a significant difference in splitting constant at any of the other positions observed; the π spin density is the same for ethyl as methyl substitution. These a_{CH_3}/a_{CH_2} ratios are much higher than reported for ethyl *vs.* propyl radicals[20a] (0.84), toluene *vs.* ethylbenzene anion radicals[20b] (0.86), *p*-methyl- *vs.* *p*-ethylphenoxy radicals[20c] (1.14), or α-hydrogen-abstracted propionic *vs.* butyric acids[20d] (1.05). The difference in ratio must involve a difference in effective *Q* values. The imide anion radicals are the only ones mentioned which have substituents next to the alkyl group large enough to cause significant conformational preference for the alkyl group. Q_B is accepted to be largely controlled[21] by the quantity $B_1 \cos^2\theta$ where θ is the dihedral angle between the C–H bond and the *p* orbital at the adjacent carbon. If R = H for XII (*i.e.*, for the N-methyl imides) there will be no conformational preference; then $\cos^2\theta = 0.5$. If R = CH$_3$, XII will be the most stable conformer; it has $\cos^2\theta = 0.25$. Propyl radical has the smallest possible substituents on the β-carbon, and shows the smallest known a_{CH_3}/a_{CH_2} ratio. Assuming no preference for the latter one predicts a limiting ratio of 1.68 for complete conformation preference of structures like XII. If some amount of conformational preference were present in propyl radical, this number would be too low. It is not necessary to invoke any effect other than conformational preference to explain the large a_{CH_3}/a_{CH_2} values observed for these N-alkyl imide anions.



XII

The "protonated" radicals from naphthalic anhydrides only form at high applied potentials, and must be reduction products of the anion radical. Simple carbonyl reduction products were ruled out by preparation of their radical anions, which are different from the "protonated" radical. We suggest that ring protonation to give VIII (the ring-protonated anion of lowest energy) or IX (that derived by protonation of the dianion at the ring site of greatest electron density (3 position)) would be most reasonable. To see if these were possible structures, we attempted HMO calculation of spin densities for VIII and IX. Arbitrarily choosing $h_O = 1.3$, $k_{C*O} = 1.3$, $k_{C'C*} = 1.2$, $h_X = 2.0$, $k_{C*X} = 1.2$, and only allowing for the saturated carbon by setting $h_C = 0.1$ for the sp^2 carbons attached to it, gave the spin densities in Table VIII. We do not believe

Table VIII. Comparison of V (X = O) "Protonated Trianion" and Calculated[a] Spin Densities for VIII and IX

Obsd[b]		
0.295		
0.216		
0.058 (*meta*)		
0.011 (*meta*)		
0.011		
	VIII	IX

[a] See text. [b] Assuming the 3.78-gauss triplet is due to a ring-protonated site. Splittings marked (*meta*) are those which disappeared in the 2,5-di-*t*-butyl analog.

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[17] K. Hausser, H. Brunner, and J. C. Jochims, *Mol. Phys.*, 10, 253 (1966).

[18] Using the 6.9-gauss methyl splitting of the methyl di-*t*-butyl analog (T. Steven and W. Waters, *Proc. Chem. Soc.*, 253 (1962)) and $Q^{H}{}_{CH_3}$ of 27 gauss for this uncharged radical.

[19] L. M. Stock and J. Suzuki, *ibid.*, 136 (1962).

[20] (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963); (b) J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, 5, 43 (1962); (c) T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 253 (1962); (d) P. Smith, J. T. Pearson, P. B. Wood, and T. C. Smith, *J. Chem. Phys.*, 43, 1535 (1965); H. Fischer, *Z. Naturforsch.*, 19a, 866 (1964).

[21] $Q_B = B_0 + B_1 \cos^2\theta$. $B_1 \approx 50$, whereas B_0 is small. A recent estimate is −3 gauss: D. H. Levy and R. J. Myers, *J. Chem. Phys.*, 43, 3063 (1965).

there is justification to attempt a more sophisticated calculation which would allow calculation of the splitting constant of the sp^3 carbons;[22] there are simply too many unknown parameters.

Obviously one should not attach too much significance to such a crude calculation, but qualitatively 3 protonation (IX) is much easier to accommodate than 1 protonation; the proton next to the sp^3 center has considerably too high a calculated spin density, but we have not reasonably accommodated this sp^3 center in the calculation. We feel that these calculations do rule out VIII, which should show three ring protons with large splittings. It is difficult to see why 3 protonation of the 1,6-di-*t*-butyl anhydride (IIB, X = O) would give a_3 (2 H) only half as large as for 2,5 or unsubstituted anhydride, but 1 protonation is definitely ruled out, for that product would have two large splittings instead of the one observed. It is possible that a completely different species was formed from IIB (X = O).

[22] D. H. Levy, *Mol. Phys.*, **10**, 233 (1966).

Electron Spin Resonance Studies on the Anion Radical of Dibenzo[*b*,*f*]thiepin

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Abstract: The anion radical of dibenzo[*b*,*f*]thiepin has been prepared in 1,2-dimethoxyethane solution by potassium metal reduction. The esr spectrum of the radical has been recorded, and proton coupling constants have been assigned to positions by examining the esr spectra of anion radicals formed from several methyl-substituted derivatives of dibenzo[*b*,*f*]thiepin.

Esr studies of the conjugative effects of sulfur in aromatic sulfide anion radicals have been limited to planar systems. Dibenzothiophene[3-5] and thioxanthone[6,7] anion radicals have esr spectra which can be best explained by assuming that the sulfur $3p_y$ orbital is responsible for sulfur π bonding. This interaction should be very dependent on the geometry of the molecule. In order to investigate the dependence on molecular geometry of sulfur π bonding in aromatic sulfide anion radicals, we felt that it would be desirable to examine the esr spectrum of the anion radical of a nonplanar aromatic sulfide.

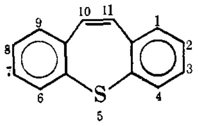
We have been unable to prepare anion radicals from diphenyl sulfide or thianthrene which are stable enough for esr studies. Dibenzo[*b*,*f*]thiepin, however, does form an anion radical which proved to be quite stable below −40°, and we decided therefore that it would be an appropriate system to examine for this study.

Results

The esr spectrum of the anion radical of dibenzo[*b*,*f*]thiepin (DBTP) is shown in Figure 1. Table I lists the coupling constants which we measured from this spectrum.

The assignment of coupling constants was done by examining the esr spectra of anion radicals prepared from 2-methyl-, 2,4-dimethyl-, 1,4-dimethyl-, and 10,11-dimethyl-DBTP. The widths of these spectra are given in Table II.

Table I. Proton Coupling Constants for the Anion Radical of Dibenzo[*b*,*f*]thiepin



Posn	A_H, gauss	Posn	A_H, gauss
1	1.41	4	1.41
2	0.00	10	3.79
3	3.79		

Table II. Widths of the Esr Spectra of Methyl-Substituted DBTP Anion Radicals

Compound	Spectral width, gauss
DBTP	20.59
2-Methyl-DBTP	20.6
2,4-Dimethyl-DBTP	21.5
1,4-Dimethyl-DBTP	23.4
10,11-Dimethyl-DBTP	38.3

Figure 2 shows the esr spectrum of the anion radical formed from 2-methyl-DBTP. It is very similar to the spectrum of the parent radical and shows no evidence for a methyl group splitting. This demonstrates that $A_2 = 0.00$ gauss.

The esr spectrum of 2,4-dimethyl-DBTP is not completely resolved, but if one examines the outer portions of the spectrum, one sees a quartet with a coupling constant of 1.4 guass, and a quartet with a coupling

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[1] Predoctoral Fellow of the National Science Foundation.

[2] To whom inquiries concerning this paper should be addressed.

[3] R. Gerdil and E. A. C. Lucken, *J. Am. Chem. Soc.*, **87**, 213 (1965).

[4] R. Gerdil and E. A. C. Lucken, *Proc. Chem. Soc.*, 144 (1963).

[5] D. H. Eargle, Jr., and E. T. Kaiser, *ibid.*, 22 (1964).

[6] E. T. Kaiser and D. H. Eargle, Jr., *J. Am. Chem. Soc.*, **85**, 1821 (1963).

[7] M. M. Urberg and E. T. Kaiser, *ibid.*, **89**, 5179 (1967).