β-Chlorostyrenes. The β-chlorostyrenes were prepared by a decarboxylation–dehydrochlorination of cinnamic acid dichloride with aqueous sodium carbonate at 100°. Pure samples of the *cis* and *trans* olefins were obtained by preparative vpc on a 10-ft × $^3/_8$-in. 30% Ucon on Chromsorb P column coated with 2% HMDS; column temperature, 165°; flow rate, 54 cc/min; retention times: *cis*, 35 min; *trans*, 53 min. The nmr data used for identification of the olefins is given in Table II.

Equilibration Studies on the β-Chlorostyrenes. No equilibration of the olefins was observed using a trace of iodine in cumene at 110° for 24 hr. Equilibration was accomplished with the *p*-anisylthiyl radical as follows. Degassed and sealed Pyrex ampoules containing the starting olefins and trace amounts of azoisobutyrylnitrile and *p*-thiocresol in cumene were allowed to react at 110° for times up to 24 hr. The *cis* olefin content was monitored by infrared measurement of a band at 1350 cm^{-1} found only in the *cis* isomer and with reference to a calibration curve derived from standard solutions. The analyses were carried out on a Beckman IR-7 spectrometer. In this way, an apparent equilibrium position of 82% *trans*- and 18% *cis*-β-chlorostyrene at 110° in cumene was found starting from either 100% *trans* or a mixture of 35.2% *trans* and 64.8% *cis* olefins.

Control Experiments. Degassed and sealed Pyrex ampoules containing 0.10 *M* β-chlorostyrene (>99.5% *trans* by vpc analysis) and 0.09 *M* *trans*-*t*-butyl α-bromopercinnamate[6] in cumene were held at 110° for 24 hr. The cooled reaction mixture was analyzed directly by vpc and found to contain a β-chlorostyrene composition of 96% *trans* and 4% *cis* olefin. In a similar experiment, a cumene solution of 0.10 *M* β-chlorostyrene and 0.08 *M* *trans*-α-chlorocinnamic acid was held at 110° for 24 hr. Vpc analysis indicated no isomerization of the *trans* olefin.

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Heterocyclic Radical Ions. I. Anion Radicals Isoelectronic with Phthalic Anhydride Anion

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received February 6, 1967*

Abstract: The esr spectra of nine radical anions isoelectronic with phthalic anhydride ion are reported; the anhydride oxygen is replaced by S, NR, and CR^-. Hückel and McLachlan calculations predict that the nature of the atom varied should not affect the phenyl ring splittings; this is experimentally verified for CH^- and NR substitution, but greater variations are observed if the atom changed formally bears two electron pairs. The *h* and *k* parameters necessary to fit the observed spectra and spin density at the group varied are discussed. Large spin density variation at this position is observed, and the CCH_3^- anion has the spin density at this position six times that at one ring position, and over half that at the other, even though $\rho_X = 0$ by symmetry considerations in the Hückel approximation.

Although quinone[1] and more recently nonaromatic 1,2-dione[2] radical anions have been extensively studied by electron spin resonance (esr), unsaturated anhydride, imide, and 1,4-diketone anions, which should also be relatively stable, have been virtually ignored. We have found that many such anions are stable enough to be conveniently produced by electrolytic reduction and studied at room temperature. Thus electrolytic reduction of maleimide in DMSO gives a transient spectrum consisting of nine main lines, which shows splittings for one nitrogen ($a_N = 2.29$ gauss) and two hydrogens ($a_N = 6.31$ gauss). Each line was an ill-unresolved doublet; we did not obtain good enough resolution to measure this NH splitting. We here report esr studies on several radical anions having the phthalic anhydride skeleton, with various substitution at the O ring position (general structure I, Table I). These anions are mostly conveniently stable for esr measurements, and have the advantage for theoretical interpretation of having two phenyl ring proton splitting constants. Better spectra were obtained in DMSO than in CH_2Cl_2, DMF, acetonitrile, or hexamethylphosphoramide. DMSO with 0.1 *M* tetrabutylammonium perchlorate as supporting electrolyte was used for the measurements reported here. The esr spectra of these compounds are of interest not only because they extend the range of structures studied, but also because of the electronic nature of the odd-electron MO. Since a node passes through the X group in the odd-electron MO, simple HMO theory predicts zero spin density at X, and unless different Coulomb and resonance integrals are employed for the carbonyls with different X groups, spin distribution independent of X. Positions with low or zero spin density by HMO theory are well known to actually have negative spin densities.[3] For such compounds the now well-known simple configuration interaction calculation of McLachlan[3] leads to much more realistic spin distributions. Study of these compounds should help to define the limitations of HMO and McLachlan calculations for interpretation of esr spectra and lead to values for the resonance and Coulomb integrals for heteroatoms necessary to correlate MO calculations with splitting constants.

Experimental Section

Phthalic anhydride, phthalimide, potassium phthalimide, and 2,3-indandione were suitably purified commercial samples. N-Dimethylaminophthalimide was prepared by the method of Drew

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

(2) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Am. Chem. Soc.*, **88**, 1998 (1966), and references therein.

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

and Hatt,[4] 2-thiophthalic anhydride by that of Reissert and Holle,[5] and 2-methylindandione by that of Wisliecenus and Kötzle.[6] N-Methyl- and -ethylphthalimides were prepared by refluxing a benzene solution of the phthalamic acid (prepared from phthalic anhydride and the aqueous amine in benzene, and dried by azeotropic separation) with thionyl chloride. Purification was by sublimation. DMSO was distilled under vacuum from calcium hydride, and tetrabutylammonium perchlorate was dried over P_2O_5 under vacuum. A Varian V-4502-12 spectrometer system was employed. *In situ* radical generation in the Varian flat electrolytic cell with applied potential varied between 0 and *ca.* 15 v was used; the spectrum was recorded at the point which gave the strongest stable signal. Samples were diluted until the best resolution possible was attained, and were deoxygenated by bubbling of nitrogen. The splitting constants determined were verified by calculation of the spectrum employing these constants. A computer program similar to Stone and Maki's[7] but modified to read out on an X–Y plotter was used. A Control Data 1604 computer was also used for MO calculations.[8]

Results

Electrolytic reduction of phthalic anhydride, 2-thiophthalic anhydride, and the substituted phthalimides gave esr spectra easily interpretable as the one-electron reduction products. The methyl splitting of N-ethylphthalimide and the dimethylamino splittings of N-dimethylaminophthalimide were not resolved, although noticeable line broadening was observed in the latter case. The spectrum for phthalimide (Figure 1) consisted of only five quintets. This is interpretable as the anion radical (If) if $a(1\ \mathrm{N}) = a(2\ \mathrm{H})$ and $a(1\ \mathrm{H}) = 2a(2\ \mathrm{H}')$. The observed line widths (*ca.* 80 mgauss, as narrow as any attained in this series) show that these relations are close to being fulfilled, but deviations of the middle three lines of each quintet from 1:1:1 intensity ratios indicate that at least the second equation is not exact. At high applied potentials the spectrum of If was replaced by a broad nine-line spectrum having proper intensity ratios to be caused by one nitrogen and two equivalent hydrogens. The same nine-line spectrum was formed by reduction of potassium phthalimide; we assign this spectrum to the deprotonated dianion radical (Ic). This was the only case in this series in which we were unable to resolve the small (a_a) benzene ring splitting: *ca.* 270-mgauss line widths were observed, the largest in this series. If wet DMSO is used as solvent, mixtures of Ic and If spectra arise when potassium phthalimide is reduced, which is further evidence that the spectra are related simply by protonation.

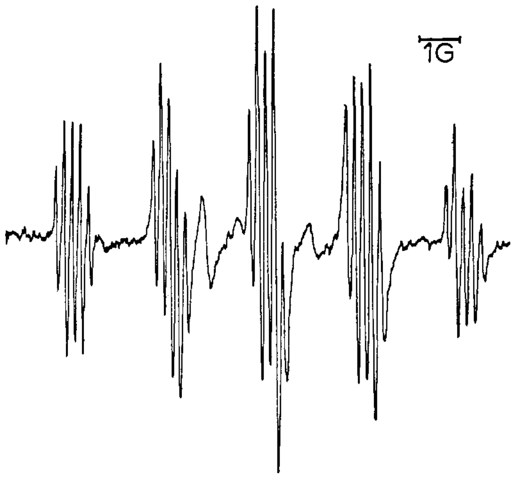
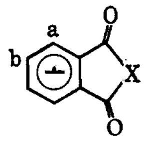


Figure 1. The esr spectrum of radical If obtained by electrolytic reduction of phthalimide in DMSO which is 0.1 *M* in tetrabutylammonium perchlorate. The small broad lines are caused by Ic.

The only spectrum observed upon reduction of 1,3-indandione showed splittings for two pairs and one single hydrogen; we assign this spectrum to the deprotonated dianion radical Id. The fact that the simple one-electron reduction product was not observed with indandione (X = CH_2), but was with phthalimide (X = NH), is not simply caused by deprotonation of the radical anion, since indandione is not a stronger acid than phthalimide.[9] We believe that the deprotonated radical is formed because it possesses a p orbital at "X" to complete the cyclic π system, and that the enolate of indandione is preferentially reduced. Similarly, only the deprotonated radical was observed upon reduction of 2-methylindandione. We write the dianion radical structure for the indandione reduction product but have not proven that one oxygen is not protonated. Proton exchange might well be rapid enough to eliminate an OH splitting, but to obtain the symmetry found, the oxygens would have to become identical within 10^{-6} sec. Since the enol is reasonably acidic and electrolysis generates base, we feel the enolate (dianion) is the more likely species to form under our conditions. Splitting constants observed for these radicals appear in Table I.

Table I. Splitting Constants (±0.02 gauss) for I Anion Radicals



I

	X	a_b (2 H)	a_a (2 H)	Other splittings
Ia	O	2.55	0.21	
Ib	S	2.15	0.31	
Ic[a]	N^-	~2.65	?	$a_N = 1.72$
Id	CH^-	2.42	0.23	$a_{HC}{}^{CH} = 0.85$ (1 H)
Ie	$CCH_3{}^-$	2.54	0.20	$a_H{}^{CH_3} = 1.33$ (3 H)
If	NH	2.40	0.205	$a_N = 2.40$, $a_{HC}{}^{NH} = 0.41$ (1 H)
Ig	NCH_3	2.41	0.24	$a_N = 2.54$, $a_H{}^{CH_3} = 0.90$ (3 H)
Ih	NCH_2CH_3	2.41	0.22	$a_N = 2.52$, $a_H{}^{CH_2} = 0.56$ (2 H)[b]
Ii[a]	$NN(CH_3)_2$	~2.42	0.22	$a_N = 2.70$, others not resolved

[a] Lines broadened by unresolved splittings. [b] Methyl splitting not resolved.

Discussion

Positional assignments of the large and small aromatic splittings were verified by obtaining the spectrum of 4-methylphthalic anhydride. Splittings of 2.58 (1 H), 2.24 (3 H), and 0.53 (1 H) gauss were observed. The remaining hydrogen splitting was not resolved, and must be small, for 90-mgauss peak-to-peak line widths were observed. Since replacement of H by CH_3 results in only a fairly small perturbation of the spin distribution, this result requires that the b hydrogens show the large splitting, as expected from MO calculations.

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(5) A. Reissert and H. Holle, *Chem. Ber.*, **44**, 3029 (1911).
(6) W. Wisliecenus and A. Kötzle, *Ann.*, **252**, 81 (1889).
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(8) We thank Professors Zimmerman and Holm for MO programs.
(9) E. Grens and G. Vanags, *Zh. Organ. Khim.*, **1**, 3 (1965).

The most notable aspect of the splittings recorded in Table I is the small variation of ring splittings. This result essentially bears out (for the benzene ring) the Hückel prediction that the nature of X should not affect the spin distribution. The compounds with formally one electron pair at X (Id–j) have remarkable similar benzene ring splittings; only the 2-methylindandione deprotonated dianion radical (Ie) has splittings outside of experimental error of being the same; its splitting at "b" is about 6% higher than the others. The anion radicals formally possessing two electron pairs at X (Ia–c) show larger deviations.

Spin density at the X position is clearly not as constant, however, as is obvious from those cases which have a spin label attached to this position. The 0.85-gauss splitting of Id ($X = CH^-$) is converted to a spin density with the most confidence, because extensive work has been done to evaluate Q_H^{CH} in the McConnell relationship, $a_H^{CH} = Q^{CH}\rho_c$. For this situation the Q_H^{CH} required is certainly in the range -23 to -30 gauss. Q_H^{CH} does, in many cases, decrease in magnitude with increased charge density.[10] Q_H^{CH} has also been predicted to increase with decreasing C–CH–C angle.[11] For pyracylene radical anion, which also has a five-membered ring with all carbons formally sp^2 hybridized, a Q near $(-)30$ gauss is required[12] to fit the esr spectrum to McLachlan calculations. These two effects would tend to cancel, and a "normal" Q_H^{CH} of *ca.* -24 might be expected for this system. This gives $\rho_X = 0.031$ for Id ($X = CH^-$). $Q_H^{CCH_3}$ has also received much study and values of *ca.* 18–20 gauss are observed for radical anions.[2,13] This indicates that $|\rho_X| = 0.067$ for Ie ($X = {}^-CCH_3$). Since $Q_H^{CCH_3}$ definitely shows a dependence on charge, decreasing in going from cation to neutral to anion radicals, and the charge density at C_X in Ie is unusually high, this calculated spin density should be a minimum value.

It is impossible as yet to interpret a nitrogen splitting constant in terms of spin distribution, for the proper Q values (up to seven can be required) have eluded evaluation.[14] The slight variation of a_N for If–Ij does show that spin in the C–NR–C portion of the molecule does vary, but the magnitude of the variation cannot be estimated (since the various Q's required are of similar magnitude but opposite sign, large variations in spin density could be concealed in these splittings).

Although no work has been done on the dependence of Q_H^{NH} with charge, values of -33.7[15] and -38.8 ± 2[16] have been suggested for cationic species. By analogy with Q_H^{CH}, relatively small differences might be expected for anionic species. Assuming $Q_H^{NH} = -35$ for If gives $\rho_X = 0.012$ ($X = NH$). Values for $Q_H^{CCH_3}$ for anion radicals have not been reported and the proportionality might well depend on charge in a fashion similar to $Q_H^{CCH_3}$. Since tetramethylhydrazine cation[17] requires a $Q_H^{NCH_3}$ of about 27 gauss, a lower value could be predicted for Ig. Then available estimates indicate $\rho_X > 0.033$ for $X = NCH_3$. These admittedly crude ρ_X estimations are summarized in Table II. We note that for carbon and nitrogen, substituting CH_3 for H raises the spin density at the position of attachment, but that $X = {}^-CR$ has significantly greater spin density than $X = NR$.

Table II. Calculated Spin Densities at X in I Systems[a]

X in I	$\lvert\rho_X\rvert$
CH^-	$\sim$0.031
CCH_3^-	$\geqslant$0.067
NH	$\sim$0.012
NCH_3	>0.033

[a] See text for derivation of the figures.

Clearly Hückel theory, with its $\rho_X = 0$ prediction, is very poor for system I. The spin density magnitude at X is experimentally up to six times that at position a, and over half that at b. Hückel calculations also give too low an a_b/a_a ratio (for the reason that ρ_a is negative by more accurate calculations). To see how successful McLachlan's treatment is for this system, calculations were carried out on I. McLachlan's value of 1.2 for his λ parameter was employed. To account for differences in the coulomb and resonance integrals in this heteroatomic system, $\alpha_y = \alpha_c + h_y\beta_c$ and $\beta_{cy} = K_{cy}\beta_{cc}$ were used in the conventional manner. Fraenkel and co-workers[18] have done extensive McLachlan calculations on semiquinones and ketyls, and they find that the parameters which fit esr spectra best vary somewhat from compound to compound. Generally h_0 values in the range 1.3–1.6 are necessary with k_{CO}/h_0 somewhat greater than one. Best $K_{C'C^*}$ values were near 1.2 for planar radicals. Small auxilliary inductive parameters (aip) of $h_C = 0.1h_0$ or $h_{C'} = -0.1$ were also employed.

McLachlan calculations on system I show that the h_X and k_{C^*X} values chosen do not affect the a and b aromatic splittings significantly; the X atom is too far away. Table III shows a comparison of experimental and calculated spin densities of Id (which has essentially the same ring splittings as If–i). With so many "adjustable" parameters much significance cannot be

Table III. Comparison of Experimental and Calculated Spin Densities for Id

Position	Exptl[a]	Calcd[b]	Calcd[c]
a	0.010	−0.010 (−0.010)	−0.009
b	0.101	0.101 (0.101)	0.100
X(CH⁻)	0.031	−0.035 (−0.018)	−0.038
O	. . .	0.121 (0.119)	0.102
C*	. . .	0.127 (0.121)	0.148
C′	. . .	0.179 (0.179)	0.178

[a] Using $Q = 24.0$. [b] $h_0 = 1.30$, $k_{C^*O} = 1.74$, $k_{C'C^*} = 1.10$, $h_X = 0.30$, $k_{CX} = 1.10$. In parentheses appear the values calculated with the same parameters except $h_X = 1.5$ (about that expected for $X = NH$ (If)). [c] $h_0 = 1.60$, $k_{C^*O} = 1.80$, $k_{C'C^*} = 1.04$, $h_X = 0.30$, $k_{C^*X} = 1.04$.

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placed upon any set which happens to fit the limited data available; we present two sets, for $h_0 = 1.3$ and $h_0 = 1.6$, which fit reasonably well; other combinations fit as well. Use of aip's $h_{C'}$ or h_{C*} would change the other parameters necessary for fit; even higher k_{C*O} values would be necessary. We do not feel our data justify introducing more parameters.

Clearly, a negative h_X is required to raise $|\rho_X|$ to the over 0.06 observed for Ie. The upward shift in $|\rho_X|$ seen upon methylation at X could be accounted for by using a lower h_X value to adjust for the C–H and C–alkyl electronegativity difference, but a hyperconjugation calculation might be more reasonable (and introduce two more "adjustable" parameters). The decrease of $|\rho_X|$ as the electronegativity of X is raised is expected; use of Streitwieser's suggested h_N value[19] of 1.5 gives a calculated ρ_N for phthalimide anion not far from that arrived at by arguing from Q values (compare Tables II and III). We are surprised at the near constancy in ρ_a and ρ_b values in this group of compounds; certainly the chemistry of enolate and amide carbonyls is so different that we had expected different h and k values to be necessary. Perhaps there are compensating changes in the many parameters necessary to describe the spin density, and the result is an artifact of this system.

To fit the two experimental splittings of the phthalic anhydride spectrum (Ia, X = 0), using $Q = 24$ again, $h_0 = 1.49$, $k_{C*O} = 1.49$, $k_{C'C*} = 1.20$ gives a reasonable fit. It may be simply accidental that the three spectra which deviate the most are those which formally have two unshared pairs of electrons at X. There is a significant shift of spin density into the benzene ring with X = S (Ib) in comparison with all the other spectra, however. Sulfur was the only third-row element studied, and some special bonding effect of the sulfur may well be involved. Lücken[20] has suggested that 3d orbital interactions of the sulfur atoms of dithiins fit the esr spectra better than just 2p interactions. The effect here is not large, and we cannot assign a mechanism for the effect of the sulfur.

McLachlan theory does not seem adequate to explain the differences observed in the I spectra in detail, but in general gives reasonable spin densities.[21]

Acknowledgment. We wish to thank the Wisconsin Alumni Research Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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[21] Since submission of this paper, R. E. Sioda and W. S. Koski, *J. Am. Chem. Soc.*, **89**, 475 (1967), have published esr spectra of phthalimide and phthalic anhydride anions in DMF, reporting splittings similar to although not identical with ours in DMSO. Our work indicates the spectrum they report for2-phenyl indandione must be for the deprotonated species. G. A. Russell, E. R. Talaty, and R. H. Horrocks, *J. Org. Chem.*, **32**, 333 (1967), report spectra for the semidiones of diacylethylenes in five- and six-membered rings.

Stable Carbonium Ions. XXXI.[1] *p*-Anisonium and Methylphenonium Ion Formation *via* Aryl Participation in Strong Acid Solution

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received January 21, 1967*

Abstract: The first observation (nmr) of arylonium ion formation *via* aryl participation in strong acid solution was achieved. The *p*-anisonium, 2,4,6-trimethylphenonium, and pentamethylphenonium ions were obtained in SbF_5–SO_2 solution at low temperature upon ionization of the corresponding β-phenylethyl chlorides. Conditions permitting bridged phenonium (arylonium) ion formation over competing classical benzylic ion (styryl cation) formation were established. The spirocyclopropylbenzenonium ion structure of phenonium ions is discussed.

Considerable interest has been focused on phenonium (arylonium) ions. In recent years it was spearheaded by Cram's[2,3] studies of phenonium ion systems and Brown's[4] suggested reexamination of this concept.

These arguments have centered largely around the nature of the cationic transition states in the rate studies of solvolysis systems and the stereochemistry of the resulting products.[5] Extensive radiolabeling studies of phenylethyl solvolysis reactions have been carried out by Collins and these have been recently reviewed.[6]

Results and Discussion

No direct observation of phenonium ion formation *via* phenyl participation from phenylethyl[7–9] or related

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