[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORIES, UNIVERSITY OF NORTH CAROLINA]

Ferrocenylazobenzenes. Resonance Interaction of Ferrocene with Substrates

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A series of substituted *m*-ferrocenylazobenzenes and *p*-ferrocenylazobenzenes was prepared and the ultraviolet and visible spectra were obtained for purposes of interpreting resonance effects of the ferrocenyl substituent on the azo substrate. Strong bathochromic shifts for the *p*-ferrocenylazobenzenes compared to slight shifts for the *m*-ferrocenylazobenzenes indicate that the ferrocenyl substituent does interact with the substrates by resonance, and the electron donating character of this interaction is seen in the greatly exalted bathochromic shift for *p*-ferrocenyl-*p*′-nitroazobenzene. The *p*-ferrocenyl substituent causes a greater shift of the azobenzene absorption than does a *p*-phenyl substituent.

The high electron density in the aromatic rings of ferrocene is reflected in the reactivity of the ferrocene nucleus toward electrophiles. As a substituent, ferrocene exhibits electron donor properties. This has been shown quantitatively in the comparison of the base constants of *m*-ferrocenylaniline (*m*-aminophenylferrocene) and *p*-ferrocenylaniline (*p*-aminophenylferrocene) with aniline in 80% aqueous alcohol reported by Nesmeyanov[2]: aniline, 7.2×10^{-11}; *m*-ferrocenylaniline, 1.4×10^{-10}; *p*-ferrocenylaniline, 2.2×10^{-10}. The same interpretation is given to the results that *p*-ferrocenylphenol is a weaker acid than phenol and the ferrocenylbenzoic acids are weaker acids than benzoic acid.

A series of *m*- and *p*-ferrocenylazobenzenes were prepared for the purpose of observing resonance effects of the ferrocenyl substituent on the azobenzene substrates as exhibited in the shifts of the absorption maxima in the ultraviolet and visible spectra. The ferrocenylazobenzenes were conveniently prepared by condensation of the appropriate nitrosobenzenes with *m*- and *p*-aminophenylferrocene. *p*-Ferrocenylazobenzene was also prepared by direct arylation of the ferrocinium ion with a diazonium salt of *p*-aminoazobenzene. Table I lists the properties of the ferrocenylazobenzenes.

TABLE I

FERROCENYLAZOBENZENES

(FC = FERROCENYL)

Compound	M.P.	Color	Yield, %	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
p-Fc	122.8–123.8	Red	49	$C_{22}H_{18}N_2Fe$	7.65	7.43
p-Fc, *p*′-Cl[a]	217.5–218.7[b]	Red	82	$C_{22}H_{17}N_2ClFe$	6.99	7.15
p-Fc, *p*′-Br	216.5–218.0[b]	Red	78	$C_{22}H_{17}N_2BrFe$	6.29	6.23
p-Fc, *p*′-I	196.0–197.5	Red	80	$C_{22}H_{17}N_2IFe$	5.69	5.89
p-Fc, *m*′-Cl	134.0–136.0	Purple	56	$C_{22}H_{17}N_2ClFe$	6.99	7.18
p-Fc, *p*′-CH_3	180.8–181.8	Red	55	$C_{23}H_{20}N_2Fe$	7.38	7.44
p-Fc, *o*′-Cl	134.0–135.5	Black	60	$C_{22}H_{17}N_2ClFe$	6.99	6.95
p-Fc, *m*′-CF_3	116.5–118.0	Purple	47	$C_{23}H_{17}N_2F_3Fe$	6.45	6.53
p-Fc, *p*′-NO_2	260 (dec.)[b]	Green[c]	58	$C_{22}H_{17}N_3O_2Fe$	10.22	10.47
m-Fc	109.8–111.8	Orange-red	64	$C_{22}H_{18}N_2Fe$	7.65	7.81
m-Fc, *p*′-Cl	118.0–119.0	Red	55	$C_{22}H_{17}N_2ClFe$	6.99	7.18
m-Fc, *p*′-Br	117.0–119.0	Red	68	$C_{22}H_{17}N_2BrFe$	6.29	6.44
m-Fc, *p*′-I	153.0–155.0	Purple	68	$C_{22}H_{17}N_2IFe$	5.69	5.74
m-Fc, *m*′-Cl	66.0– 68.5	Red	39	$C_{22}H_{17}N_2ClFe$	6.99	7.16
m-Fc, *p*′-NO_2	166.0–168.0	Brown	45	$C_{22}H_{17}N_3O_2Fe$	10.22	10.38

[a] Calcd. for $C_{22}H_{17}N_2ClFe$: C, 65.94; H, 4.28. Found: C, 65.83, 65.60; H, 4.31, 4.46. [b] Uncorrected. [c] Reddish purple in solution.

DISCUSSION

The ultraviolet and visible spectra of the *p*-ferrocenylazobenzenes (Table II) show marked resonance interaction[3] between the *p*-ferrocenyl substituent and the azo system as reflected in the strong bathochromic shifts of the absorption maxima compared to the corresponding parent azobenzenes. *p*-Ferrocenylazobenzene, itself, shows maximum absorption in the ultraviolet at 350 mμ

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[1] Union Carbide Fellow, 1958–59.

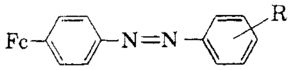
[2] A. N. Nesmeyanov, E. G. Perevalova, and R. V. Golovnya, *Doklady Akad. Nauk S.S.S.R.*, **103**, 81 (1958); A. N. Nesmeyanov, *Proc. Roy. Soc., London*, **246**, 495 (1958).

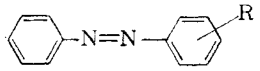
[3] A referee has pointed out that resonance interactions of phenyl substituents with the ferrocene ring have been previously reported and that many of these same conclusions were drawn in these reports: K. L. Rinehart, 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959, Abstracts, p. 29; M. Cais and R. T. Lundquist, XVIIth International Congress of Pure and Applied Chemistry, Munich, August 1959, Abstracts p. 7.

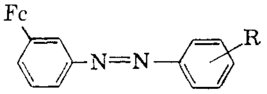
TABLE II

ULTRAVIOLET AND VISIBLE SPECTRA OF FERROCENYLAZOBENZENES

(Fc = ferrocenyl)







R	U.V. Max., mμ	ϵ	Vis. Max., mμ	ϵ	R	U.V. Max., mμ	ϵ	Vis. Max., mμ	ϵ	R	U.V. Max., mμ	ϵ	Vis. Max., mμ	ϵ
p-H	350	25100	488	4640	*p*-H	316	21200	441	519	*p*-H	317	23400	438	1420
					p-C_6H_5	342	30600	440	1030					
p-Cl	357	27600	499	5300	*p*-Cl	322	23900	442	623	*p*-Cl	325	25000	442	1530
p-Br	358	29100	500	5460	*p*-Br	324	25500	442	638	*p*-Br	326	26300	442	1610
p-I	361	31500	502	5730	*p*-I	329	27400	443	740	*p*-I	332	27600	442	1700
p-CH_3	353	28800	483	4950	*p*-CH_3	323	23800	439	676					
p-NO_2	376	25900	537	6080	*p*-NO_2	331	25500	457	638	*p*-NO_2	331	25000	450	1550
o-Cl	359	24500	506	5140	*o*-Cl	322	18600	450	481					
m-Cl	356	26000	504	5090	*m*-Cl	319	21700	443	499	*m*-Cl	319	22300	443	1350
p-Cl	357	27600	499	5300	*p*-Cl	322	23900	442	623					
m-CF_3	357	25100	507	5040	*m*-CF_3	315	21400	443	458					

compared to 316 mμ for azobenzene, a shift of 34 mμ. By comparison, the phenyl substituent in *p*-phenylazobenzene shifts the maximum of azobenzene to 342 mμ, a shift of 26 mμ, indicating a greater resonance interaction for the ferrocenyl substituent than for the phenyl group. In *m*-ferrocenylazobenzene, on the other hand, the ferrocenyl substituent cannot interact with the azo function, and, as expected, there is but a slight shift of the maximum absorption (317 mμ, a shift of one mμ) from that of azobenzene.

Similar effects are seen in the visible spectra, where the *p*-ferrocenyl substituent causes a bathochromic shift in the azobenzene absorption of 47 mμ, compared to slight hypsochromic shifts of 1 mμ for *p*-phenylazobenzene and 3 mμ for *m*-ferrocenylazobenzene.

It is interesting to compare the absorption maxima and extinction coefficients of ferrocenylazobenzene to those of ferrocene and azoferrocene. While ferrocenylazobenzene absorbs at 350 mμ (ϵ 25,100) in the ultraviolet and at 488 mμ (ϵ 5300) in the visible, ferrocene itself absorbs at the shorter wave lengths, 326 mμ and 440 mμ, with much smaller extinction coefficients, 50 and 87, respectively.[4] Nesmeyanov *et al.*, have prepared azoferrocene,[5] and have reported absorptions at 315 mμ (ϵ 350), 375 mμ (ϵ 76), and 510 mμ (ϵ 81).

Table II shows that ultraviolet extinction coefficients of the substituted azobenzenes are increased by the ferrocenyl substituent. Except for the ferrocenyl-*p*′-nitroazobenzenes, which show abnormally low extinction coefficients, the *p*-ferrocenyl group increases the extinction coefficients between 14 and 30%, while the *m*-ferrocenyl substituent appears responsible for smaller increases ranging from 1 to 10%. Similarly, the visible extinction coefficients of the substituted azobenzenes are between seven- and eleven-fold larger due to the *p*-ferrocenyl substituent, while the *m*-ferrocenyl group is responsible for extinction coefficients around 2.5 times larger than the correspondingly substituted azobenzenes not containing ferrocene.

Table III lists the spectral shifts brought about by substituents within the two series, the azobenzenes and the *p*-ferrocenylazobenzenes. From the listed data it can be seen that for those substituents with electron withdrawing inductive effects, the bathochromic shifts in the *p*-ferrocenylazobenzene series are slightly larger than the corresponding shifts in the azobenzene series. The only group with an electron donating inductive effect, the methyl group, shows a smaller shift in the *p*-ferrocenyl series. This suggests that the *p*-ferrocenyl group is electron releasing in its resonance interaction with the azo system. The effect is dramatic in the case of the *p*-nitro group, the only substituent listed that is electron withdrawing by resonance as well as by induction. The bathochromic shift in *p*-nitro-*p*′-ferrocenylazobenzene is far larger than the shifts caused by other substituents in the *p*-ferrocenyl series (26 mμ), and, relative to azobenzene, the shift is 60 mμ.

It can be seen from Table III that the *m*-CF_3 group also causes a marked bathochromic shift in both the ultraviolet and visible spectra of the *p*′-ferrocenylazobenzene series, though not so outstandingly large as that of the *p*-nitro group.

In the *m*-ferrocenylazobenzene series (Table II) the absorption maxima for the substituted *m*-ferrocenylazobenzenes are very nearly the same as the correspondingly substituted azobenzenes.

The magnitudes and directions of these spectral shifts suggest activated states that can be represented by the structures:

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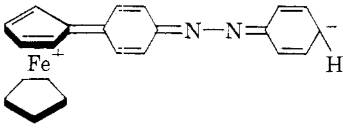
(4) G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 2125 (1952).

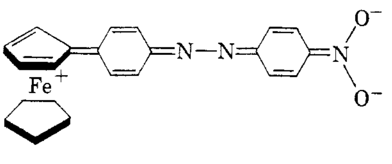
(5) A. N. Nesmeyanov, E. G. Perevalova, and T. V. Nikitina, *Tetrahedron Letters*, **1**, 1 (1960).

TABLE III

SPECTRAL SHIFTS ARISING FROM SUBSTITUENTS IN AZOBENZENE AND p'-FERROCENYLAZOBENZENE

	Ultraviolet			Visible		
Group	a, Observed shift of azobenzene spectrum, mμ	b, Observed shift of p'-ferrocenylazobenzene spectrum, mμ	b − a	c, Observed shift of azobenzene spectrum, mμ	d, Observed shift of p'-ferrocenylazobenzene spectrum, mμ	d − c
p-Cl	6	7	+1	1	11	+10
p-Br	8	8	0	1	12	+11
p-I	13	11	−2	2	14	+12
p-CH_3	7	3	−4	−2	−5	−3
p-NO_2	15	26	+11	16	49	+33
o-Cl	6	9	+3	9	18	+9
m-Cl	3	6	+3	9	16	+7
p-Cl	6	7	+1	1	11	+10
m-CF_3	−1	7	+8	2	19	+17





where the substituted ring takes on the character of a diene-iron complex.[6]

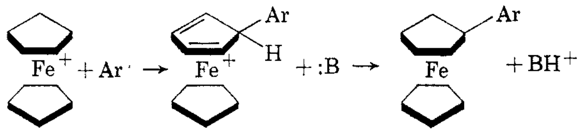
The use of the arylation of the ferrocinium ion in the direct preparation of p-ferrocenylazobenzene and m-nitrophenylferrocene from diazonium salts has led the authors to comment on the mechanism of this reaction as presented by Pauson.[7] Pauson has shown that traces of neutral ferrocene are necessary for the initiation of this reaction according to the mechanism:

$$Fc + ArN_2^+ \longrightarrow Fc^+ + Ar^\cdot$$

$$Ar^\cdot + Fc^+ \longrightarrow Fc^+Ar + H^\cdot$$

$$H^\cdot + Fc^+ \longrightarrow Fc + H^+$$

A more plausible modification of this scheme can be suggested wherein a base attack on the intermediate sigma complex, rather than loss of a hydrogen atom, is proposed[8]:



EXPERIMENTAL

Melting points are corrected.

p-Aminophenylferrocene and m-aminophenylferrocene. p-Aminophenylferrocene was prepared by hydrogenation of p-nitrophenylferrocene[10] with platinum oxide in alcohol at room temperature and 50 lb. pressure. The reduction required about 20 min. and crystallization from alcohol gave 90% yield of a product melting at 159–160°. Nesmeyanov[10] reported p-aminophenylferrocene from a tin–hydrochloric acid reduction of p-nitrophenylferrocene, m.p. 159–160.5°.[11] m-Aminophenylferrocene was prepared by hydrogenation of m-nitrophenylferrocene in a similar manner, m.p. 117–118°; reported[10] m.p. 112–113°. The benzoyl derivative of m-aminophenylferrocene was prepared, m.p. 207.0–209.5°.

Anal. Calcd. for $C_{23}H_{19}ONFe$: N, 3.68. Found: N, 3.82.

Nitrosobenzenes. Three methods were used for the preparation of substituted nitrosobenzenes. *Method 1.* Substituted nitro compounds were reduced to hydroxylamines with zinc and ammonium chloride, followed by oxidation to nitroso compounds with ferric chloride or dichromate.[12–14] This method was used for the preparation of nitrosobenzene, p-chloronitrosobenzene, p-bromonitrosobenzene, p-iodonitrosobenzene, and o-chloronitrosobenzene.

Method 2. Substituted aromatic amines were oxidized with Caro's acid.[14,15] This method was used for m-chloronitrosobenzene, p-methylnitrosobenzene, and m-trifluoromethylnitrosobenzene.

Method 3. p-Nitronitrosobenzene was prepared by peracetic acid oxidation of p-nitroaniline.[16]

Azobenzenes. The azobenzenes were prepared by dissolving equimolar quantities (usually about 0.004 mole) of the appropriate substituted aniline and the substituted nitroso compound in glacial acetic acid. The azo compounds were collected as precipitates after standing from 12 to 48 hr., and were recrystallized from water and alcohol. The compounds prepared from nitrosobenzene and the appropriate substituted anilines were: m-chloroazobenzene, m.p. 68–

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(6) Pauson has reported stable diene-iron complexes, though of a somewhat different nature from this, P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

(7) P. L. Pauson, *Quart. Revs. (London)*, **9**, 391 (1955).

(8) Rinehart[9] has discussed the nature of the intermediate sigma complexes in electrophilic substitution of ferrocene. While he has represented the intermediates as resonance forms with the seat of positive charge located principally in the rings, we prefer to represent these intermediates with the positive charge largely contained in the iron, in view of Pauson's stable diene-iron complexes.[6]

(9) K. L. Rinehart, K. L. Motz, and S. Moon, *J. Am. Chem. Soc.*, **79**, 2750 (1957).

(10) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and L. S. Shilovtseva, *Doklady Akad. Nauk S.S.S.R.*, **102**, 535 (1955).

(11) V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3012 (1955).

(12) W. J. Wijs, S. E. Hoekstra, R. M. Ulmann, and E. Havinga, *Rec. trav. chim.*, **77**, 746 (1958).

(13) R. E. Lutz and M. R. Lytton, *J. Org. Chem.*, **2**, 68 (1937).

(14) C. H. Coleman, C. M. McCloskey, and F. A. Stuart, *Org. Syntheses*, Coll. Vol. III, 668 (1955).

(15) E. Bamberger and R. Hubner, *Ber.*, **36**, 3803 (1903).

(16) E. Hecker, *Ber.*, **88**, 1666 (1955).

69.5°, reported[17] m.p. 67.5°; *p*-chloroazobenzene, m.p. 88–89°, reported[17] m.p., 87.5°; *p*-bromoazobenzene, m.p. 88–90°, reported[17] m.p. 89°; *p*-iodoazobenzene, m.p. 105–107°, reported[18] m.p. 105°; *p*-methylazobenzene, m.p. 69–71°, reported[19] m.p. 71–72°; *p*-phenylazobenzene, m.p. 154–155°, reported[20] m.p. 150°, and *m*-trifluoromethylazobenzene, m.p. 38–39°, reported[21] m.p., 37°.

The azobenzenes prepared from aniline and the appropriate substituted nitrosobenzenes were: *p*-nitroazobenzene, m.p. 132–134°, reported[11] m.p. 134–135°; *m*-trifluoromethylazobenzene, m.p. 38–39°; and *o*-chloroazobenzene, m.p. 29–31°.

Anal. Calcd. for $C_{12}H_9N_2Cl$: C, 66.52; H, 4.19. Found: C, 66.60, 66.79; H, 4.28, 4.17.

Ferrocenylazobenzenes. The ferrocenylazobenzenes were prepared by the same methods as the azobenzenes, using in each case the aminophenylferrocene and a 10% excess of the appropriate nitroso compound. Their properties and analyses are listed in Table I. The ferrocenylazobenzenes dissolve in alcohol to give colored solutions varying from orange to reddish purple. They are soluble in concd. hydrochloric acid to form red solutions.

p-Ferrocenylazobenzene was also prepared directly from ferrocene and *p*-aminoazobenzene. A solution of 9.3 g. (0.05 mole) of ferrocene was prepared in 27 ml. of concd. sulfuric acid, to yield the ferrocinium ion, and this solution was poured on crushed ice. To this solution was added a solution of diazotized *p*-aminoazobenzene in acetic acid, prepared from 9.9 g. (0.05 mole) of *p*-aminoazobenzene in acetic acid with sulfuric acid and a 10% excess of sodium nitrite at −3°. The mixture was brought to room temperature with stirring overnight. Work-up involved chromatography on alumina (benzene). *p*-Ferrocenylazobenzene was obtained in 21% yield, based on recovery of 38% of the ferrocene. The infrared spectrum of this product was identical with that prepared from *p*-aminophenylferrocene; a mixed melting point showed no depression.

Several nitroso compounds failed to couple with the aminophenylferrocenes. *p*-Nitroso-*N*,*N*-dimethylaniline, *p*-nitrosoanisole, and *m*-nitrosotoluene yielded with the amino compounds intractable tars.

Attempts to diazotize *m*-aminophenylferrocene and *p*-aminophenylferrocene and to couple with *N*,*N*-dimethylaniline failed. In both cases it is doubtful that the diazonium salt was obtained. This is not surprising in view of the report of failures by Nesmeyanov[22] to diazotize *p*-aminophenylferrocene.

Spectra. The spectra were obtained with a Cary Model 14 instrument. The solutions were prepared in absolute alcohol in about $10^{-5}M$ for the ultraviolet spectra and about $10^{-4}M$ for the visible spectra and were allowed to stand overnight in the dark to assure the *trans* form of the azo compounds. Although attempts to detect *cis* and *trans* isomers of the ferrocenylazobenzenes by chromatography on alumina gave no evidence of these two types of isomers, it was deemed desirable to allow these solutions to stand in the dark overnight in view of reports of changes in the spectra of azobenzenes upon exposure to light.[23,24] In view of experience the authors have had with decomposition of solutions of acetylferrocene and other derivatives of ferrocene on standing in acetonitrile, the ferrocenylazobenzene solutions were examined for decomposition on standing. No changes were observed in either the absorption maxima or the extinction coefficients of these solutions over a period of several days.

Acknowledgment. The authors would like to thank the University of North Carolina Research Council for financial assistance with some of the analyses.

Chapel Hill, N. C.

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(17) E. Bamberger, *Ber.*, **29**, 102 (1896)

(18) E. Noelting and P. Werner, *Ber.*, **23**, 3252 (1903).

(19) C. Mills, *J. Chem. Soc.*, **67**, 925 (1895).

(20) P. Greiss, *Ber.*, **9**, 132 (1876).

(21) V. P. Chernetskii, L. M. Vagupolskii, and S. B. Serebryanyi, *Zhur. Obshcheĭ Khim.*, **25**, 2161 (1955); *Chem. Abstr.*, **50**, 8661 (1956).

(22) A. N. Nesmeyanov, E. G. Perevalova, L. S. Shilovtseva, and Yu A. Ustynyuk, *Doklady Akad. Nauk S.S.S.R.*, **124**, 331 (1951).

(23) W. R. Brode, J. H. Gould, and G. M. Wyman, *J. Am. Chem. Soc.*, **74**, 4641 (1952).

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[Contribution from the Department of Chemistry, Duke University]

Alkali Catalyzed Aldol Condensation of Bisacetylferrocene with Benzaldehyde to Form Mono- and Dibenzaldehyde Derivatives[1]

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Treatment of mixtures of bisacetylferrocene and benzaldehyde with 5% aqueous-ethanolic sodium hydroxide produced a yellow product and a red product, which were evidently mono- and dibenzaldehyde derivatives respectively. The structure of the red product was established as the dibenzal derivative of bisacetylferrocene but that of the yellow product was not determined. Some evidence was obtained that the latter compound had a cyclic vinyl ether structure.

It has previously been shown[3] that acetylferrocene (I) and benzaldehyde undergo the alkali catalyzed aldol type of condensation accompanied by the elimination of water to form the benzal derivative II.

It therefore seemed possible that bisacetylferrocene (III)[4] and benzaldehyde would undergo this

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(1) Supported in part by the Office of Ordnance Research, U. S. Army.

(2) Esso Research and Engineering Company Fellow, 1957–1958.

(3) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

(4) We are indebted to Dr. R. L. Pruett, Union Carbide Chemicals Company, South Charleston, W. Va., for a generous sample of this compound.