Chromogens based on Non-benzenoid Aromatic Systems. Part II.[1] Arylazo-derivatives of 1,2,3,4-Tetrachlorocyclopentadiene

By **John Griffiths** * and **Martin Lockwood**, Department of Colour Chemistry, The University, Leeds LS2 9JT

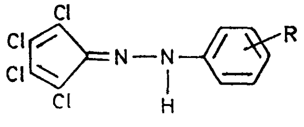
Several arenediazonium salts have been coupled to 1,2,3,4-tetrachlorocyclopentadiene and the products have been shown by i.r. spectroscopy to exist exclusively as hydrazones in the solid state. The visible absorption spectra show that the same situation exists in solution, and the effect of substituents on the spectra can be interpreted most readily in terms of the hydrazone structures. In the presence of bases the hydrazones readily form anions which absorb at longer wavelengths than the parent compounds. The long wavelength bands of the anions exhibit an opposite substituent effect to that observed for the hydrazones, and the shifts of the hydrazone bands due to ionisation are approximately proportional to the Hammett σ constants of substituents in the aryl ring.

Of the few non-benzenoid aromatic analogues of azobenzene that have been studied, those based on cyclopentadiene and its derivatives have been relatively neglected with respect to their electronic absorption spectra. Cyclopentadiene,[2] diazocyclopentadiene,[3] and pyridinium cyclopentadienide [4] are known to couple with diazonium salts to give highly coloured derivatives, but little is known of the light absorption properties of the products. The only related system to receive such attention is that obtained by coupling diazonium ions to triphenylphosphonium cyclopentadienide, but the effect of substituents on the visible absorption spectra are still not fully understood.[5] Because of the possible tautomeric equilibrium between arylazocyclopentadienes and cyclopentadienone hydrazones, analogous derivatives can be made by the action of arylhydrazines on cyclopentadienones. The same products can also be made by the reaction between aryl-lithiums and diazocyclopentadienes. However, although several compounds have been made by these methods, none of their visible absorption spectroscopic properties has been reported. As part of our study of chromogens based on non-benzenoid aromatic systems, we were interested in examining compounds of this type for comparison with conventional azobenzene dyes.

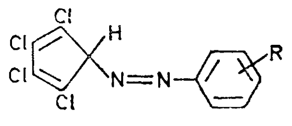
Following the work of Roedig and Hörnig, who showed that 1,2,3,4-tetrachlorocyclopentadiene coupled readily with diazonium salts,[6] this diene was chosen for further study because of the stability of the derived products, a property not shown by the corresponding derivatives of cyclopentadiene.

RESULTS AND DISCUSSION

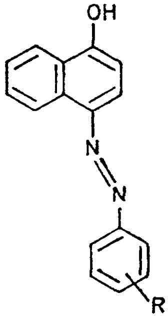
Tautomerism of the 1-*Arylazo*-2,3,4,5-*tetachlorocyclopentadienes*.—Roedig and Hörnig [6] obtained good yields of the derivatives (I; R = H or *p*-NO_2) by treating 1,2,3,4-tetrachlorocyclopentadiene with the appropriate diazotised arylamine under anhydrous acidic conditions. We have observed that equally effective coupling can be achieved under neutral aqueous conditions, provided



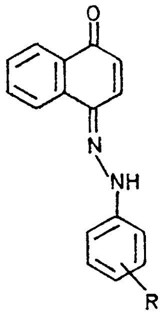
(I)



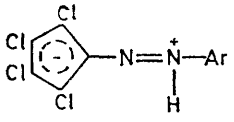
(II)



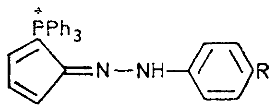
(III)



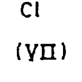
(IV)



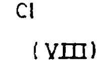
(V)



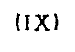
(VI)



(VII)



(VIII)



(IX)

---

[1] Part I, J. Griffiths, *J. Chem. Soc.* (*B*), 1971, 801.

[2] A. Leibner and O. Laue, *Ber.*, 1906, **39**, 2026; A. P. Terent'ev and L. L. Gomberg, *J. Gen. Chem. U.S.S.R.*, 1938, **8**, 662 (*Chem. Abs.*, 1939, **33**, 12,857).

[3] D. J. Cram and R. D. Partos, *J. Amer. Chem. Soc.*, 1963, **85**, 1273.

[4] D. Lloyd and J. S. Sneezum, *Tetrahedron*, 1958, **3**, 334.

[5] F. Ramirez and S. Levy, *J. Org. Chem.*, 1956, **21**, 1333; *J. Amer. Chem. Soc.*, 1957, **79**, 6167; *J. Org. Chem.*, 1958, **23**, 2035; S. C. Sehgel and A. V. Patwardham, *Indian J. Chem.*, 1970, **8**, 900.

[6] A. Roedig and L. Hörnig, *Chem. Ber.*, 1955, **88**, 2003.

sufficient ethanol is present to dissolve the diene. In this way coupling can be carried out with solutions of the diazonium chloride prepared in the usual way from the arylamine in dilute hydrochloric acid. The derivatives (I; R = *p*-OMe, *p*-Me, H, *p*-Cl, *m*-Cl, *m*-NO_2, *p*-Ac, or *p*-NO_2) were prepared thus in yields of 67—98%, and were isolated as orange-red solids, stable at room temperature but decomposing on melting. All were very soluble in most organic solvents.

The derivatives (I; R = H or *p*-NO_2) had previously been examined by Roedig and Hörnig, and were assigned the hydrazone structures (I) rather than the tautomeric azo-structures (II; R = H or *p*-NO_2) as their i.r. spectra showed strong N–H absorptions characteristic of hydrazones. However, the possible existence of stable azo-tautomers in other substituted derivatives cannot be discounted on the basis of these observations alone, as several instances are known where the equilibrium between azo and hydrazone tautomers is markedly affected by substituents. Thus for example in the 4-arylazo-1-naphthol system (III) $\rightleftharpoons$ (IV) the derivative (III; R = *p*-OMe) exists almost exclusively in the azo-form in aqueous ethanol, whereas (IV; R = *p*-Cl) exists entirely in the hydrazone form in the same solvent.[7]

The eight derivatives (I), which have substituents with a wide range of electron-donating or -withdrawing effects, were thus examined in the solid state (KBr) by i.r. spectroscopy. All showed strong N–H absorption at *ca.* 3200 cm^{-1}, indicating predominantly hydrazone structures. The same result was obtained for solutions of (I) in 95% ethanol on the basis of their electronic absorption spectra. By analogy with arylazoalkanes, the azo-tautomers (II) should absorb in the region 390—400 nm (log ε *ca.* 2·2), whereas in fact (Table 1) all absorbed in the region 400—440 nm (log ε 4·29—4·65), which is to be expected for the more conjugated hydrazone structures. No evidence for secondary absorption in the former region could be found, and thus the hydrazone form (I) must be considerably more stable than the azo-form (II), irrespective of aryl substituents. This contrasts then markedly with other systems capable of azo–hydrazone tautomerism and it is interesting that in another non-benzenoid analogue of the azobenzenes, the 5-phenylazotropolones,[1] where stable hydrazone tautomers might have been expected, only the azo-tautomeric forms could be detected by i.r. or u.v. spectroscopy.

TABLE 1

Visible spectra of compounds (I) and anions (VIII) in 95% ethanol

R	σ	$\lambda_{max.}$/nm (log ε) (I)	$\lambda_{max.}$/nm (VIII) [a]	$\Delta\lambda$/nm [b]
p-OMe	−0·16	440 (4·46)	453	13
p-Me	−0·15	425 (4·50)	451	26
H	0	414 (4·48)	450	36
p-Cl	0·24	416 (4·50)	458	42
m-Cl	0·37	416 (4·29)	458	42
m-NO_2	0·70	402 (4·48)	460	58
p-Ac	0·87 [c]	415 (4·60)	499	84
p-NO_2	1·24 [c]	418 (4·65)	542	124

[a] Determined with solutions containing (I) (5×10^{-5}M) and potassium hydroxide (2×10^{-2}M) in 95% ethanol. [b] $\lambda_{max.}$ (VIII) − $\lambda_{max.}$ (I). [c] Enhanced (σ^*) values.

Visible Absorption Spectra in Neutral and Alkaline Solution.—The tetrachlorocyclopentadienone hydrazones (I) are expected, by analogy with simpler hydrazones, to have a long wavelength absorption band corresponding to migration of charge from the amino-group into the five-membered ring. In this respect the cyclopentadiene ring behaves as an electron acceptor, and this may be crudely depicted in resonance terms by the process (I) $\xrightarrow{h\nu}$ (V), implying a greater contribution of (V) in the excited state than in the ground state. The cyclohexadienone ring in hydrazones (IV) plays a similar role in their long wavelength transitions.

In general agreement with this it is found (Table 1) that the wavelength maxima move to shorter wavelengths as the electron-withdrawing power of the aryl substituents R in (I) increases. A regular variation of $\lambda_{max.}$ with the Hammett substituent constants (σ) is not observed, particularly with strong electron-withdrawing groups.

The observed range of absorption maxima (400—440 nm) suggests that the electron acceptor properties of the tetrachlorocyclopentadiene ring are relatively weak in comparison with other acceptors commonly encountered in hydrazone dyes. Thus, for example, both the 4-arylazo-1- (IV) and the 1-arylazo-2-naphthols (in their tautomeric hydrazone forms) absorb in the range 450—500 nm. However, the derivatives (VI; R = H, NO_2, or $NHEt_2^+$) do exhibit absorption bands similar to (I), at 420—440 nm.[5]

The general decrease in the $\lambda_{max.}$ values of (I) with increasing σ provides further evidence for the assigned hydrazone structures (I).

Because of resonance stabilisation of the anions (VII) $\longleftrightarrow$ (VIII), the hydrazones (I) are particularly acidic. This is indicated by the intense reversible colouration of their solutions when treated with small amounts of alkali. Roedig and Hörnig noted that the derivatives (I; R = H or *p*-NO_2) dissolved slowly in aqueous sodium hydroxide to give yellow solutions.[6] It seems likely that under these conditions hydrolysis is occurring, as we have observed that addition of alkali to the yellow solutions of these derivatives in ethanol gave instantaneous colour changes, to red-orange in the case of (I; R = H) and to magenta in the case of (I; R = *p*-NO_2). The solutions of the anions (VII) or (VIII) were stable at room temperature, and readily reverted to the neutral form on acidification. The absorption spectra of the anions in ethanolic solution are summarised in Table 1. The absorption spectrum of the most acidic member of the series of hydrazones, *i.e.* (I; R = *p*-NO_2), showed no evidence for anion formation in neutral solution, and thus (I) are appreciably less acidic than the 5-phenylazotropolones, which readily ionise in solution.[1] The deep colouration of the *p*-nitrophenylhydrazone of

---

[7] A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 1953, 1443.

2,3,4,5-tetraphenylcyclopentadienone in alkali had been noted,[8] but was not examined further.

The bathochromic shift accompanying ionisation of hydrazones (I) is also found with simpler hydrazone derivatives.[9] The $\lambda_{\text{max.}}$ values of the anions (Table 1) show a reverse substituent dependence to those of (I), and the visible bands move to longer wavelengths as the electron-withdrawing strength of aryl substituents R increases. Since the anions and hydrazones are isoelectronic this implies that the ground states of the two species differ markedly in charge distribution, and structure (VIII) is probably a better representation of the charge distribution in the anions than (VII). The substituent effect in the anions suggests that the long wavelength transition involves some degree of charge migration into the aryl ring, and in this respect they resemble negatively substituted azobenzenes. The visible absorption bands of other systems capable of azo–hydrazone tautomerism show opposite substituent effects for their anionic and neutral forms [*e.g.* hydrazones (IV) and their anions].[10]

TABLE 2

Yields and properties of hydrazones (I)

R	Yield (%)	M.p. (°C) [a]	$\nu_{\text{max.}}$(KBr)/ cm^{-1}
p-OMe	67	126—128	3200
p-Me	93	150—152	3200
H	95	132—133	3200
p-Cl	98	146—148	3210
m-Cl	84	151—152	3200
m-NO_2	92	179—180	3220
p-Ac	84	202—204	3200
p-NO_2	74	188—190	3220

[a] Uncorrected. All derivatives melt with decomposition.

The general range of absorption shown by anions (VIII) (451—542 nm), can be compared with those of other substituted azobenzenes. The ionised *p*-phenylazophenols containing similar substituents absorb at somewhat shorter wavelengths, in the region 400—500 nm, whereas the anions of the 1-arylazo-2-naphthols show a closer resemblance, absorbing in the range 460—580 nm.

TABLE 3

Analytical data for hydrazones (I)

	Found (%)					Required (%)			
R	C	H	N	Cl	Formula	C	H	N	Cl
p-OMe	42·45	2·35	8·25	41·9	$C_{12}H_8Cl_4N_2O$	42·6	2·4	8·3	41·95
p-Me	44·8	2·5	8·7	44·0	$C_{12}H_8Cl_4N_2$	44·7	2·4	8·85	43·95
H	42·7	1·95	9·05	45·8	$C_{11}H_6Cl_4N_2$	42·9	2·0	9·1	46·0
p-Cl	38·55	1·55	7·95	51·4	$C_{11}H_5Cl_5N_2$	38·6	1·5	8·2	51·8
m-Cl	38·8	1·65	8·4	51·5	$C_{11}H_5Cl_5N_2$	38·6	1·5	8·2	51·8
m-NO_2	37·7	1·55	11·8	40·1	$C_{11}H_5Cl_4N_3O_2$	37·4	1·4	11·9	40·15
p-Ac	44·55	2·25	7·80	40·85	$C_{13}H_8Cl_4N_2O$	44·6	2·3	8·0	40·5
p-NO_2	37·3	1·6	11·7	39·8	$C_{11}H_5Cl_4N_3O_2$	37·4	1·4	11·9	40·15

A few other phenylazo-derivatives of cyclopentadienide anions are known, all of which are stabilised by the presence of positive substituents in the five-membered ring, *e.g.* (IX; $R = PPh_3^{+}$[5] or N_2^{+}[3]). These are made by coupling diazonium salts to the corresponding cyclopentadienide. The visible absorption spectra of (IX; $R = PPh_3^{+}$) have been reported,[5] and the maxima fall in the range 450—525 nm, which is similar to that observed for the anions (VIII).

The colour change of the hydrazones (I) in alkali is another example of halochromism, and for theoretical reasons[11] the wavelength shift between the two forms (I) and (VIII) should show a better linear correlation with the Hammett substituent σ constants than do the individual wavelength maxima of hydrazones (I) or their anions (VIII). The correlation coefficient r for the plot of $\lambda_{\text{max.}}$ (I) against σ was found to be $-0{\cdot}53$, indicating a very poor correlation. Plots of $\lambda_{\text{max.}}$ (VIII) were somewhat better ($r = 0{\cdot}87$), but the correlation between $\lambda_{\text{max.}}$ (VIII) $-$ $\lambda_{\text{max.}}$ (I) showed a marked improvement ($r = 0{\cdot}96$), in general agreement with the theoretical prediction. The relationship between the wavelength shift ($\Delta\lambda$) and σ can be expressed in the form (1).

$$\Delta\lambda = 67\sigma + 27 \text{ nm } (r = 0{\cdot}96) \qquad (1)$$

EXPERIMENTAL

Visible absorption spectra were recorded with a Unicam SP 800 spectrophotometer and i.r. spectra with a Unicam SP 200 spectrophotometer. The visible spectra of (I) were determined for solutions in 95% ethanol and the spectra of the anions (VIII) were determined for solutions of (I) (5×10^{-5}M) in the same solvent containing potassium hydroxide (2×10^{-2}M).

Synthesis of Hydrazones (I).—The yields, m.p., and i.r. spectral properties of the eight derivatives (I) are summarised in Table 2, and the analytical data in Table 3. In a typical experiment the arylamine (5 mmol) was dissolved in concentrated hydrochloric acid (1·3 ml), diluted with water (15 ml), and treated with a solution of sodium nitrite (5 mmol) at 0—5°. The solution of the diazonium salt was added dropwise to a stirred solution of 1,2,3,4-tetrachlorocyclopentadiene (5 mmol) in ethanol (40 ml), maintaining the temperature below 5°. After 1 h the suspension was warmed to room temperature and stirred overnight. Water (20 ml) was added and the solid was filtered off and dried. In every case t.l.c. showed that the product consisted of a single compound. Recrystallisation from benzene–ligroin gave analytically pure crystalline solids.

We thank the S.R.C. for a research studentship (to M. L.).

[3/069 *Received*, 11*th January*, 1973]

---

[8] N. O. V. Sonntag, S. Lindlar, E. I. Becker, and P. E. Spoerri, *J. Amer. Chem. Soc.*, 1953, **75**, 2283.

[9] L. A. Jones and C. K. Hancock, *J. Org. Chem.*, 1960, **25**, 226; H. H. Jaffé, H. L. Jones, and M. Isaks, *J. Amer. Chem. Soc.*, 1964, **86**, 2934.

[10] J. Griffiths, *J. Soc. Dyers and Colourists*, 1972, **88**, 106.

[11] A. Weller, 'Progress in Reaction Kinetics,' ed. G. Porter, Pergamon, London, 1961, p. 187.