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SPECTROSCOPIC AND STRUCTURAL STUDIES OF SOME OXOCARBON CONDENSATION PRODUCTS—I

PREPARATION AND CHARACTERIZATION OF SOME SUBSTITUTED PHENAZINES AND QUINOXALINES

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Abstract—The preparation of 22 mono- and 4 poly-condensation products of 5- and 6-membered ring oxocarbons and various *o*-phenylenediamines are reported. The products are characterized by their proton NMR spectra in various solvents and their vibrational mull spectra in the region from 3700 to 1300 cm^{-1}.

INTRODUCTION

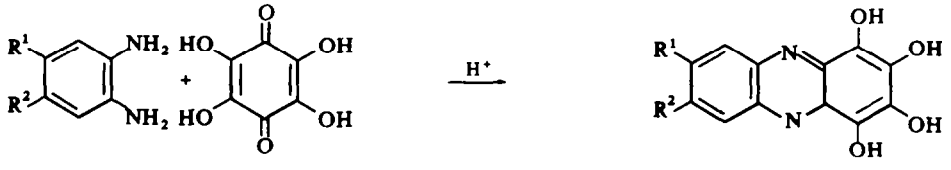
VARIOUS condensation products have been isolated from the reaction between monocyclic polycarbonyl compounds, the so-called oxocarbons,[1] and *o*-phenylenediamines[2–5] and ethylenediamine.[6] The structures of the condensation products have been postulated almost entirely on the basis of analytical data. Whilst recent work has led to the isolation of several of these compounds, their structural ambiguities have not been resolved.[7]

We have obtained condensation products from the reaction between 5 and 6-membered ring oxocarbons and various *o*-phenylenediamines. The resulting products may be considered as derivatives of either quinoxaline or phenazine.

RESULTS AND DISCUSSION

Tetrahydroxy-*p*-benzoquinone condenses with *o*-phenylenediamines to yield high melting, sparingly soluble solids. These may be formulated as 1,2,3,4-tetrahydroxyphenazines (Diag. 1; I–VI).

DIAG. 1



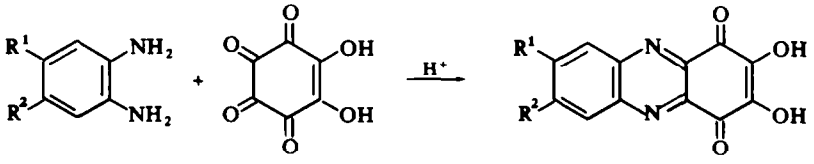
I: $R^1 = R^2 = H$;
II: $R^1 = H$, $R^2 = CH_3$;
III: $R^1 = R^2 = CH_3$;

IV: $R^1 = H$, $R^2 = Cl$;
V: $R^1 = H$, $R^2 = COOH$;
VI: $R^1 = H$, $R^2 = NO_2$

The condensation between rhodizonic acid and *o*-phenylenediamines also produces high melting, sparingly soluble solids, which may be formulated as 2,3-

dihydroxyphenazine-1,4-quinones (Diag. 2; VII–XII). Triquinoyl octahydrate and *o*-phenylenediamines condense to give hydrated monocondensation products which may tentatively be considered as phenazine 1,2,3,4-tetrones (Diag. 3; XIII–XVII. These compounds appear to be slightly contaminated with polycondensation products. With excess *o*-phenylenediamine the tricondensation products, diquinoxalino (2.3-*a*,2′.3′-*c*) phenazines (XXIII and XXIV) are obtained, which supports the hexaketonic structure of triquinoyl octahydrate.

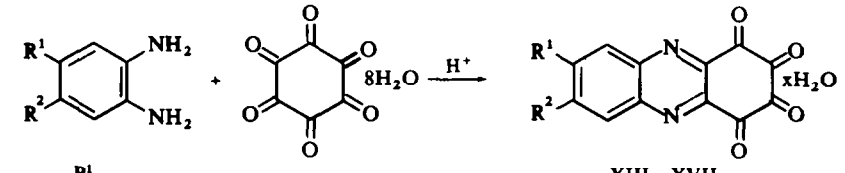
DIAG. 2



VII: $R^1 = R^2 = H$;
VIII: $R^1 = H$, $R^2 = CH_3$;
IX: $R^1 = R^2 = CH_3$;

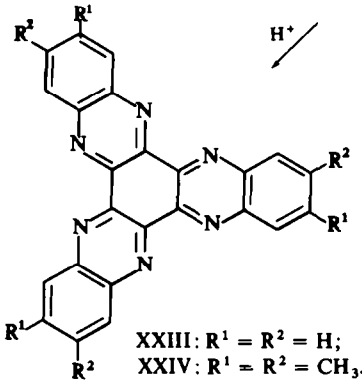
X: $R^1 = H$, $R^2 = Cl$;
XI: $R^1 = H$, $R^2 = COOH$;
XII: $R^1 = H$, $R^2 = NO_2$

DIAG. 3



XIII—XVII

XIII: $R^1 = R^2 = H$;
XIV: $R^1 = H$; $R^2 = CH_3$;
XV: $R^1 = R^2 = CH_3$;
XVI: $R^1 = H$; $R^2 = COOH$;
XVII: $R^1 = H$; $R^2 = Cl$.



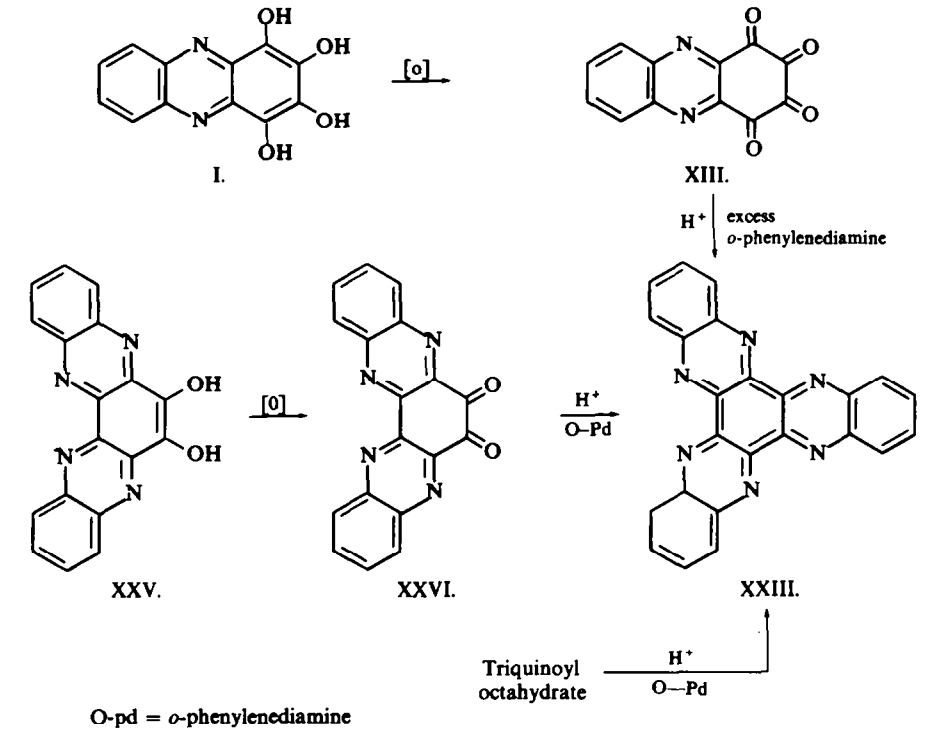
XXIII: $R^1 = R^2 = H$;
XXIV: $R^1 = R^2 = CH_3$.

The phenazine tetrones can also be obtained by oxidizing the corresponding tetrahydroxy-phenazines. The inter-relationship between the various 6-membered ring oxocarbon condensation products was established by a series of reactions starting with tetrahydroxyphenazine, triquinoyl octahydrate and the di-condensation product quinoxaline (2.3-*a*)-3,4-dihydroxy phenazine (XXV; Diag. 4).

Similar condensation products (XVIII–XXII) are obtained from the 5-membered ring oxocarbons croconic acid and leuconic acid (Diag. 5).

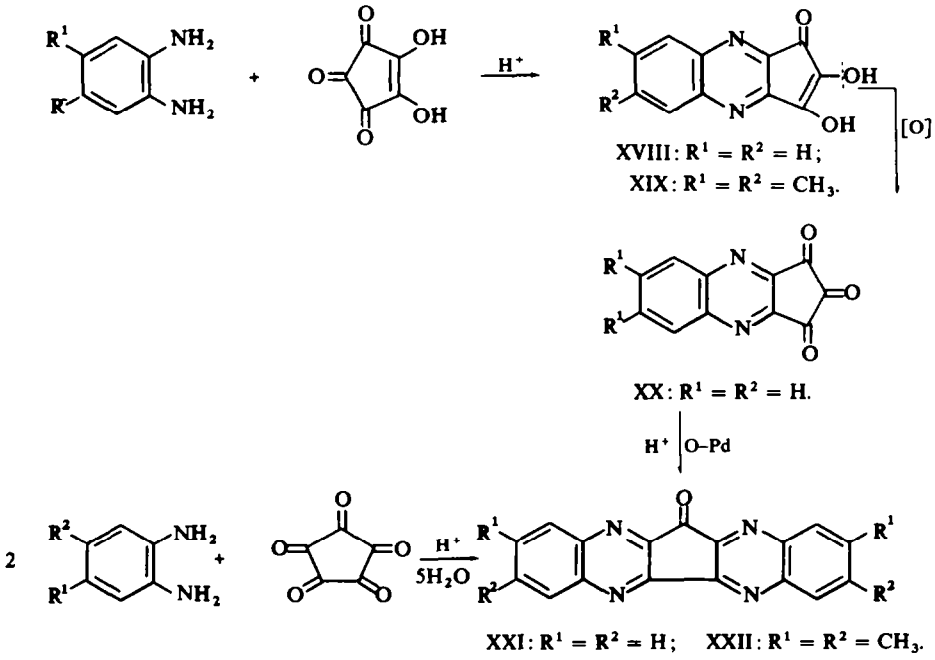
Structural characterization studies have been carried out on these condensation products using proton NMR, vibrational and electronic spectroscopy[8] and mass spectrometry.[9]

DIAG. 4



O-pd = *o*-phenylenediamine

DIAG. 5



Proton NMR spectra. In many cases the low solubility of the condensation products presented difficulties in obtaining the NMR spectra. The most suitable solvents were found to be DMSO and pyridine (PY). The details of the NMR spectra are summarised in Table 1. The proton NMR spectrum of tetrahydroxy phenazine(I) has a symmetrical multiplet ring pattern centred at $\tau = 2{\cdot}13$ which is comparable to the

TABLE 1. PROTON NMR DATA FOR SOME OXOCARBON CONDENSATION PRODUCTS[a]

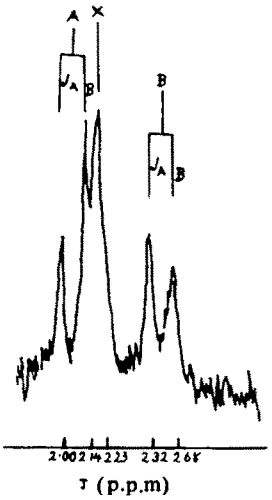
Compound	Ring protons	Hydroxyl protons	Methyl protons	Other protons
1,2,3,4 tetra hydroxyphenazine I	1·82–2·42 m 2·13c (DMSO)	4·16 (~24 Hz)[b] (DMSO)		
7-methyl derivative II	2·0–2·68 m (DMSO)		7·61 (PY)	
7,8 dimethyl derivative III	2·23 (DMSO)		7·69 (PY)	
7-chloro derivative IV	1·98–2·58 m (DMSO)	1·5 vb (DMSO)		
7-carboxyl derivative V	1·49–2·17 m (DMSO)	1·6 vb (DMSO)		
7-nitro derivative VI	1·39–2·26 m (DMSO)	1·4 vb (DMSO)		
2,3 dihydroxy phenazine 1,4 quinone VII	1·54–2·01 m (DMSO) 1·78c	4·89 (PY)		
7-methyl derivative VIII	1·68–2·15 m (DMSO)	4·85 (PY)	7·51 (PY)	
7,8 dimethyl derivative IX	2·15 (DMSO)	4·81 (PY)	7·69 (PY)	
7-chloro derivative X	1·52–2·02 m (DMSO)	4·83 (PY)		
7-carboxyl derivative XI	1·48–2·03 m (DMSO)	4·76 (~42 Hz)[b] (PY) 6·30 vb (DMSO)		
7-nitro derivative XII	0·83–1·34 m (DMSO)	4·85 (PY) 5·95 vb (DMSO)		
7-methylphenazine 1,2,3,4 tetrone XIV	1·65–2·14 m (DMSO)		7·62 (PY)	5·0 (~24 Hz)[b] (DMSO)
7,8 dimethyl derivative XV	1·98 (DMSO) 1·87 (dioxan)		7·68 (PY)	5·16 (~90 Hz)[b] (DMSO)
7-carboxyl derivative XVI	1·13 1·47 (DMSO)			4·41 (~10 Hz)[b] (DMSO)
	0·94 1·48 (dioxan)			4·75 (~20 Hz)[b] (dioxan)
7-chloro derivative XVII	1·43–1·95 m (DMSO) 1·48–2·07 m (dioxan)			5·55 (~26 Hz)[b] (DMSO) 3·63 (~12 Hz)[b] (dioxan)
Quinoxalino (2.3-*a*)-3,4 dihydroxyphenazine XXV	1·46–2·14 (DMSO) 1·80c			
6,7,6′,7′ tetramethyl diquinoxalino (2.3-2′, 3′-*b*,*d*) Cyclopentadiene-1-one. XXII	1·94 ($CDCl_3$) 1·96 (DMSO)		7·45 ($CDCl_3$) 7·68 (DMSO)	
6,7-6′,7′-tetramethyl diquinoxalino-(2,3-2′3′-*a*,*c*)-7,8 dimethyl phenazine XXIV	1·57 ($CDCl_3$)		7·35 ($CDCl_3$)	

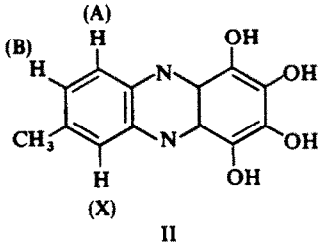
[a] All chemical shifts are on the τ scale.
[b] Signal width at half-height.
m = multiplet; c = centre of multiplet; vb = very broad.

A_2B_2 pattern centered at $\tau = 2{\cdot}10$ in the chloroform solution spectrum of phenazine.[10, 11] A similar ring proton multiplet centered at $\tau = 1{\cdot}78$ is found in the spectrum of 2,3 dihydroxy-phenazine-1,4-quinone(VII). The deshielding effect on the ring protons of replacing the 1,4-OH groups by the more electronegative CO groups is thought to be responsible for the A_2B_2 pattern occurring at lower field in VII than in I. A similar effect is observed in the ring spectra of the 7,8-dimethyl derivatives which consist of a single peak. In DMSO it occurs at $\tau = 2{\cdot}23$, $\tau = 2{\cdot}15$ and $\tau = 1{\cdot}98$ for the tetrahydroxyphenazine(III) the quinone(IX) and the tetrone(XV) respectively.

In the derivatives monosubstituted at the 7 position the ring proton spectrum may be analysed as an ABX system (Diag. 6). This applies to the 1,2,3,4 tetrahydroxy phenazines (II–VI), the 2,3-dihydroxyphenazine 1,4-quinones (VIII, X, XI, XII) and the phenazine 1,2,3,4-tetrones (XVI and XVII).

DIAG. 6





II

The effect of a Me group substituted in the ring is not expected to deshield the remaining ring protons to the same extent as will the N atoms in the adjacent ring. On this basis the low-field doublet in the ring proton spectrum of the methyl-tetrahydroxyphenazine(II) is assigned to proton A, the high-field doublet to proton B and the centre peak to proton X. A similar assignment has been reported for the ring protons of 2,8-dimethoxyphenazine.[10] The ring proton spectra of the other 7-substituted phenazines have been analysed in the same manner the results of the analysis are reported in Table 2. In general the effect of the 7-chloro substituent is to deshield protons B and X more than A such that the signals from protons A and X lie close to each other making the spectral analysis more difficult. The strongly electron withdrawing nitro and carboxyl groups increase the deshielding of the X proton such that its signal is the one at lowest field. Unfortunately these substituents also tend to reduce the solubility of the compounds in solvents suitable for NMR.

With the exception of 7-carboxyl-2,3 dihydroxy-phenazine-1,4 quinone (XI) the values found for the spin-coupling constant J_{AB} are comparable with those reported for phenazine, 8·819 Hz,[11] and both 2,8-dimethoxyphenazine[10] and 2,8-dichlorophenazine[12] 9 Hz. In the spectrum of 7-methyl-2,3-dihydroxy-phenazine-1,4-quinone

TABLE 2. CHEMICAL SHIFTS AND SPIN COUPLING CONSTANTS FOR THE RING PROTONS IN THE 7-SUBSTITUTED PHENAZINES

Compound number	Proton chemical shifts[a]			Spin couplings constants[b]	
	A	B	X	J_{AB}	J_{BX}
II	2·08	2·58	2·23	~8·4	
IV	2·06	2·50	2·12	~8·4	
V	2·07	1·94	1·47	8·4–9·0	~1·2
VI	2·18	1·73	1·41	~8·4	~2·4
VIII	1·77	2·06	1·86	~8·4	~1·8
X	1·61	1·90	~1·52	~9	~3
XI	~1·60	~1·99	~1·48	~4·8	
XII	~1·32	~1·28	~0·85		
XIV	1·74	2·03	1·83	~9	~2·4
XVI in DMSO	integrated areas of the peaks at τ 1·13 and 1·47 are in the ratio 1:2				
XVII in DMSO	1·54	1·82	~1·44	~10·2	~2·4
XVII in dioxan	1·62	1·96	~1·50	~9·6	~2·1

[a] Chemical shifts on the τ scale.

[b] Spin coupling constants in Hz.

(VIII) there is an indication of a very small spin-coupling constant between the *para* protons A and X. This should be compared with the reported values of 0·202 Hz in phenazine[11] and between 0·0 Hz and 0·7 Hz in benzene derivatives.[13] It was not possible to unambiguously determine J_{AX} from any of the spectra reported here.

The signal from the protons of the Me groups generally occurs between $\tau = 7{\cdot}5$ and 7·7 which agrees with data reported from numerous methyl-substituted heterocyclic molecules.[14]

The broad signal centered at $\tau = 4{\cdot}16$ in 1,2,3,4-tetrahydroxy phenazine (I) is attributed to the OH protons. Whilst remaining broad this signal is found to shift to lower fields upon ring substitution at the 7 and 8 positions, possibly indicating an increase in H-bonding. The solvent dependence of this signal is shown by the spectra of the 7-carboxyl (XI) and the 7-nitro-phenazine 1,4-quinones (XII) in DMSO and PY. With the exception of 7-carboxyl-phenazine 1,4-quinone (XI) the other derivatives give fairly sharp signals in PY solution in the range $\tau = 4{\cdot}76$ to $\tau = 4{\cdot}89$, the broad signal (half-width ~42 Hz) found for this compound could be due to rapid proton exchange between the enolic and carboxylic groups.

The tetrones (XIV–XVII) give broad signals in DMSO solution between $\tau = 4{\cdot}41$ and $\tau = 5{\cdot}55$ these are most probably due to the water molecules present in these compounds.

The only other oxocarbon condensation products that were sufficiently soluble to give NMR spectra were the dicondensation products 6,7-6′,7′-tetramethyldiquinoxalino(2.3-2′.3′-*b*,*d*)-cyclopentadiene-1-one (XXII) and quinoxalino(2.3-*a*)-3,4-dihydroxyphenazine (XXV) and the tricondensation product 6,7-6′,7′-tetramethyldiquinoxaline(2.3-2′.3′-*a*,*c*)-7,8-dimethylphenazine (XXIV). The spectrum of XXII gives a single ring proton line at $\tau = 1{\cdot}94$ in $CDCl_3$ and at $\tau = 1{\cdot}96$ in DMSO, with some indication of spin coupling between the inequivalent *para* protons J_{HH} ~1 Hz. The anticipated A_2B_2 ring proton pattern is found, centered at $\tau = 1{\cdot}80$, in the spectrum of XXV in DMSO solution. The tricondensation product (XXIV) in $CDCl_3$ exhibits a signal at $\tau = 1{\cdot}57$ and another at $\tau = 7{\cdot}35$ whose integrated areas are in the expected ratio of 1:3.

IR spectra. The details of the IR mull spectra in the region from 3700 to 1300 cm^{-1} are summarized in Table 3.

TABLE 3. IR DATA FOR SOME OXOCARBON CONDENSATION PRODUCTS BETWEEN 3700 AND 1300 cm^{-1}

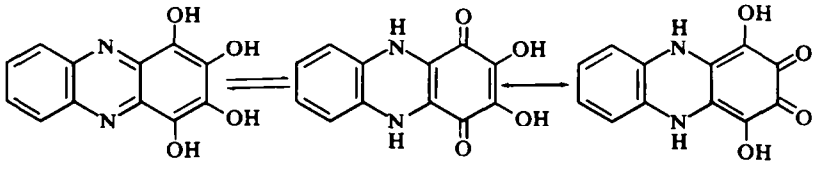
Compound	Absorption bands in cm^{-1}
I	3500–2800(b) 3380(s) 3240(s) 1650(m) 1625(m) 1610(m) 1545(s) 1475(s) 1410(s) 1395(s) 1335(m)
II	3650–2700(b) 3430(m) 3310(s) 3120(m) 1650(m) 1555(s) 1535(s) 1470(m) 1390(s) 1360(s)
III	3500–2600(b) 3450(s) 3415(s) 3330(s) 3040(s) 1670(m) 1630(m) 1555(s) 1530(s) 1455(m) 1415(s) 1395(s) 1335(s)
IV	3600–2850(b) 3220(s) 1660(m) 1630(s) 1590(s) 1530(m) 1480(m) 1405(s) 1365(m) 1315(m)
V	3640–2400(b) 3230(s) 3070(s) 1705(s) 1635(m) 1615(m) 1560(s) 1490(m) 1420(s) 1400(s) 1365(s) 1300(s)
VI	3650–2500(b) 3480(s) 3270(s) 3100(s) 3080(s) 1645(m) 1590(s) 1515(m) 1480(m) 1415(m) 1335(s) 1300(s)
VII	3325(s) 3140–2500(mb) 3075(m) 3000(m) 1690(m) 1665(s) 1640(s) 1575(m) 1545(m) 1500(s) 1375(s) 1325(s) 1310(s)
VIII	3400–2700(b) 3310(s) 3050(m) 1655(s) 1630(s) 1530(s) 1495(m) 1410(m) 1360(s)
IX	3640–2500(b) 3610(s) 3520(s) 3350(s) 2975(s) 1680(s) 1660(s) 1620(s) 1525(m) 1485(m) 1455(m) 1390(m) 1365(s) 1335(s) 1310(s)
X	3660–2500(b) 3520(m) 3315(m) 3050(m) 1655(s) 1620(s) 1530(m) 1480(m) 1380(s) 1355(s) 1300(s)
XI	3640–2200(b) 3590(s) 3330(s) 3050(s) 1680(s) 1655(s) 1635(s) 1535(m) 1365(s) 1320(s)
XII	3680–2300(b) 3630(s) 3520(s) 3100(m) 3080(m) 3050(m) 1650(s) 1620(s) 1555(s) 1535(m) 1460(m) 1370(s) 1330(s)
XIII	3435(s) 3140(s) 2810(m) 1730(vs) 1520(m) 1495(s) 1470(m) 1410(m) 1365(s)
XIV	3550(s) 3480(s) 3350(s) 3140(m) 1750(s) 1615(m) 1530(m) 1505(m) 1410(m) 1390(m) 1365(s)
XV	3650–2700(b) 3630(m) 3560(s) 3420(s) 3300(s) 1750(s) 1630(m) 1530(m) 1495(s) 1480(m) 1465(m) 1395(m) 1370(s) 1310(m)
XVI	3650–2400(b) 3465(s) 3175(s) 2640(m) 1745(s) 1725(s) 1660(m) 1540(m) 1435(m) 1370(s) 1310(m)
XVII	3700–2600(b) 3520(s) 3470(s) 3090(s) 2780(m) 1745(s) 1635(m) 1605(m) 1530(m) 1490(s) 1450(m) 1395(s) 1360(s) 1310(m)
XVIII	3650(m) 3150(s) 3110(s) 3020(s) 2890(m) 1725(s) 1710(s) 1655(m) 1615(s) 1570(s) 1520(s) 1490(s) 1455(s) 1440(s) 1370(s) 1318(s)
XIX	3500(s) 3190(s) 3015(m) 2920(m) 2850(m) 2770(m) 1720(m) 1705(m) 1610(s) 1540(s) 1500(s) 1425(s) 1390(m) 1360(m) 1305(s)
XX	3505(s) 3090(s) 2860(m) 2730(m) 1780(s) 1775(m) 1755(s) 1545(m) 1510(m) 1500(s) 1370(s) 1330(m)
XXI	3070(m) 1770(m) 1745(s) 1735(m) 1590(m) 1570(m) 1550(m) 1510(s) 1475(m) 1410(m) 1365(s)
XXII	3040(m) 2995(w) 2950(m) 2920(m) 1740(s) 1630(m) 1575(m) 1545(m) 1490(s) 1470(m) 1410(m) 1380(m) 1355(s)
XXIII	3070(m) 1525(m) 1500(s) 1480(m) 1410(m) 1370(s) 1345(s)
XXIV	3530(s) 3475(s) 3045(m) 2970(m) 2955(m) 2925(m) 2860(m) 1640(m) 1525(m) 1495(s) 1485(s) 1460(s) 1370(s)
XXV	3600–2400(b) 3550(m) 3370(s) 3250(s) 3070(s) 1690(m) 1665(m) 1610(m) 1570(m) 1540(s) 1495(s) 1440(m) 1375(m)
XXVI	3600–3000(b) 3450(s) 3270(s) 1740(s) 1530(m) 1505(s) 1375(s) 1350(m) 1300(m)

b = broad
s = strong
m = medium intensity
w = weak.

The broad absorption bands occuring between 3700 and 2400 cm^{-1} in the spectra of the substituted tetrahydroxy phenazines (I–VI), and the 2,3-dihydroxy-phenazine-1,4-quinones (VII–XII), are indicative of either intramolecular or intermolecular H-bonding. No specific assignments can be made for these compounds in the 1700 to 1300 cm^{-1} region since bands due to N—H and O—H deformations and C=O and ring stretching vibrations are all expected to occur.[15]

In common with similar N-heteroaromatic compounds the tetrahydroxyphenazines may exist as lactim-lactam tautomers.[16] (Diag. 7). It has been claimed that 2-hydroxyphenazine exhibits this form of tautomerism whereas the 1-hydroxyphenazine does not.[17] However Corbett[18] has demonstrated that the medium to strong intensity bands in the 1640 to 1620 cm^{-1} region are observed both in derivatives that could exhibit tautomerism and in those that definitely have the lactim structure.

DIAG. 7



lactim form lactam-forms

All of the phenazine-1,2,3,4-tetrone derivatives (XIII–XVII) are obtained as hydrates, consequently some of the CO groups may be hydrated to the *gem*-diol form. The presence of both free O—H vibrations and H-bonded ones are indicated by the absorption bands in the region from 3700 to 2400 cm^{-1}. The intense bands in the 1750 to 1730 cm^{-1} region may be assigned to the ring C=O vibrations. The strong band at 1725 cm^{-1} in the spectrum of the carboxylic acid derivative (XVI) may be assigned to the carboxyl C=O stretching vibration in comparison with 1705 cm^{-1} for the corresponding vibration in the carboxylic acid derivative of 1,2,3,4-tetrahydroxyphenazine (V).

Quinoxalino[2.3-*d*]2,3-dihydroxy cyclopentadiene-1-one (XVIII) and its Me derivative (XIX) are obtained as hydrates. The free O—H stretching band is observed at 3650 cm^{-1} in the spectrum of XVIII and at 3500 cm^{-1} in the spectrum of (XIX). The strong absorption bands in the region from 3200 to 2850 cm^{-1} indicate the presence of H-bonding. The doublets at 1725, 1710 cm^{-1} in the spectrum of XVIII and at 1720, 1705 cm^{-1} in the spectrum of XIX are probably due to Fermi resonance between the C=O fundamental and an overtone or combination band.

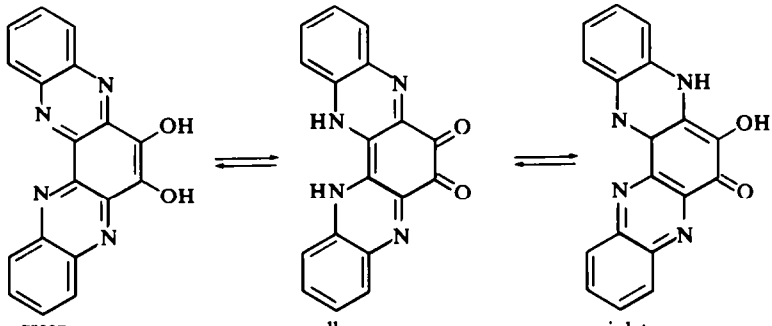
Quinoxalino[2.3-*d*]cyclopentane-1,2,3-trione (XX) is formed as the monohydrate. Three bands are observed at 1780, 1770 and 1755 cm^{-1} in the C=O absorption region which could be accounted for on the basis of a hydrated structure similar to that of ninhydrin.

The dicondensation products obtained from leuconic acid and *o*-phenylenediamines, (XXI and XXII), have strong absorption bands at 1745 and 1740 cm^{-1} respectively. An additional two bands are found in this region for XXI at 1770 and 1735 cm^{-1} probably arising from Fermi resonance.

The spectrum of the tricondensation product of triquinoyl octahydrate and *o*-phenylenediamine (XXIII) has a band at 3070 cm^{-1} which may be assigned to the C—H stretching vibrations and bands at 1525–1500 cm^{-1} and 1480 cm^{-1} which are thought to be due to skeletal ring vibrations. The corresponding hexamethyl derivative (XXIV) crystallizes as the dihydrate. The O—H absorption bands are observed at 3530 and 3475 cm^{-1}. The band occurring at 3045 cm^{-1} may be assigned to the ring C—H vibration and the bands in the region from 2970 to 2860 cm^{-1} to the C—H vibrations of the Me groups.

Eistert *et al.*[7] have reported the isolation of the dark green quinoxalino(2.3-*a*)3,4-dihydroxyphenazine (XXV) and its yellow and violet tautomers which led them to postulate the equilibrium shown in diagram 8, although they did not report the IR

DIAG. 8



green yellow violet

data of the green form. We have observed a broad band pattern in the spectrum of the green form in the region from 3600 to 2400 cm^{-1}, which is indicative of H-bonding between the O—H and C=O groups (Table 3). The yellow tautomer exhibits a sharp band at 3333 cm^{-1} which has been assigned to N—H vibrations, whereas the violet form has a broad absorption band from 3450 to 2950 cm^{-1}.[7] The medium intensity band at 1690 cm^{-1} in the green form could be due to C=O vibrations by analogy with the strong band at 1740 cm^{-1} in the corresponding dione (XXVI) (Table 3). The absorption bands at 1667 and 1637 cm^{-1} respectively in the yellow and violet tautomers have been attributed to C=O vibrations.[7]

EXPERIMENTAL

Preparation of the 1,2,3,4-tetrahydroxyphenazines

The general procedure used for the preparation of the tetrahydroxyphenazines may be illustrated by the method used for the preparation of 1,2,3,4-tetrahydroxyphenazine itself.

(a) 1,2,3,4-*Tetrahydroxyphenazine* (I). Tetrahydroxy-*p*-benzoquinone dihydrate (0·5 g, 0·0024 mole) was dissolved in hot dil AcOH (10% v/v), and a soln of *o*-phenylenediamine (0·26 g, 0·0024 mole) in hot dil AcOH was also prepared.

The two solns were mixed and allowed to cool. The green-black ppt was collected by filtration and washed thoroughly with water, ethanol, acetone and ether, yield 0·5 g (85%), m.p. ~300° dec. (Found: C, 59·27; H, 3·37; N, 11·28%. Calc. for $C_{12}H_8N_2O_4$: C, 59·02; H, 3·30; N, 11·47%).

(b) 7-*Methyl*-1,2,3,4-*tetrahydroxy-phenazine monohydrate* (II), yield 88%, m.p. 255–260° dec. (Found: C, 56·21; H, 4·56, N, 9·99%. Calc. for $C_{13}H_{10}N_2O_4H_2O$: C, 56·52, H, 4·38; N, 10·14%).

(c) 7,8-*Dimethyl*-1,2,3,4-*tetrahydroxy-phenazine* (III), yield 85%; m.p. 285–295° dec. (Found: C, 61·62; H, 4·49; N, 9·80. Required for $C_{14}H_{12}N_2O_4$: C, 61·76; H, 4·44; N, 10·29%).

(d) 7-*Chloro*-1,2,3,4-*tetrahydroxy-phenazine hemihydrate* (IV), yield 76%; m.p. 283–287° dec. (Found: C, 50·27; H, 2·87; N, 9·86. Required for $C_{12}H_7N_2O_4Cl.\ \frac{1}{2}H_2O$: C, 50·10; H, 2·80; N, 9·74%).

(e) 7-*Carboxyl*-1,2,3,4-*tetrahydroxy-phenazine monohydrate* (V), yield 81%; m.p. 295–300° dec. (Found: C, 51·13; H, 3·33; N, 9·33. Required for $C_{13}H_8N_2O_6H_2O$: C, 50·99; H, 3·29; N, 9·15%).

(f) 7-*Nitro*-1,2,3,4-*tetrahydroxy-phenazine dihydrate* (VI), yield 77%; m.p. 215° dec. (Found: C, 44·04; H, 3·60; N, 13·00. Required for $C_{12}H_7N_3O_6\ 2H_2O$: C, 44·31; H, 3·41; N, 12·92%).

The general procedure used for the preparation of the dihydroxy-phenazine-quinones may be illustrated by the method used for the preparation of 2,3-dihydroxy-phenazine-1,4-quinone itself.

(a) 2,3-*Dihydroxy-phenazine*-1,4-*quinone* (VII). Rhodizonic acid dihydrate (0·5 g, 0·0024 mole) was dissolved in water (10 ml) and *o*-phenylenediamine was dissolved in warm H_2SO_4 (10 ml, 25% w/v). The two solns were mixed and allowed to cool to room temp. The red ppt was collected by filtration and washed with water, ethanol, acetone and ether, yield 0·36 g (61%); m.p. ~280–290° dec. (Found: C, 59·65; H, 2·58; N, 11·92. Calc. for $C_{12}H_6N_2O_4$; C, 59·51; H, 2·49; N, 11·57%).

(b) 7-*Methyl*-2,3-*dihydroxy-phenazine*-1,4-*quinone* (VIII), yield 63%; m.p. ~300° dec. (Found: C, 60·78; H, 3·23; N, 10·77. Calc. for $C_{13}H_8N_2O_4$: C, 60·94; H, 3·15; N, 10·93%).

(c) 7,8-*Dimethyl*-2,3-*dihydroxy-phenazine*-1,4-*quinone dihydrate* (IX), yield 78%, m.p. >310°. (Found: C, 55·13; 55·19; H, 3·86; 4·57; N, 9·37; 8·24. Required for $C_{14}H_{10}N_2O_4\ 2H_2O$: C, 54·90; H, 4·61; N, 9·15%).

(d) 7-*Chloro*-2,3-*dihydroxy-phenazine*-1,4-*quinone dihydrate* (X), yield 74%; m.p. >310°.(Found: C, 46·94; H, 2·62; N, 9·19. Required for $C_{12}H_5N_2O_4Cl.\ 2H_2O$: C, 46·09; H, 2·90; N, 8·96%).

(e) 7-*Carboxyl*-2,3-*dihydroxy-phenazine*-1,4-*quinone hydrate* (XI), yield 83%; m.p. 280° dec. (Found: C, 50·48; H, 3·90; N, 9·13. Required for $C_{13}H_6N_2O_6H_2O$ C, 51·32; H, 2·65; N, 9·23%).

(f) 7-*Nitro*-2,3-*dihydroxy-phenazine*-1,4-*quinone dihydrate* (XII), yield 61%; m.p. 295° dec. (Found: C, 43·87; 45·33; H, 3·32; 3·23; N, 12·96; 13·18. Required for $C_{12}H_5N_3O_6\ 2H_2O$: C, 44·59; H, 2·81; N, 13·00%).

The phenazine-tetrones were prepared from the corresponding tetrahydroxy-phenazines.

(a) *Phenazine*-1,2,3,4-*tetrone dihydrate* (XIII). Phenazine I (2 g) was added in small portions to an ice-cooled stirred HNO_3 soln (20 ml, 65% w/v). After the reaction was complete, the yellow solid was filtered off and washed with cold water, ethanol, acetone and ether, yield 2·25 g (quantitative), m.p. 190° dec. (Found: C, 52·03; H, 2·74; N, 10·30. Calc. for $C_{12}H_4N_2O_4\ 2H_2O$ C, 52·18; H, 2·92; N, 10·14%).

(b) 7-*Methyl-phenazine*-1,2,3,4-*tetrone tetrahydrate* (XIV). Phenazine II (1·1 g) was added in small portions to an ice-cooled stirred HNO_3 soln (25 ml, 50% v/v). After the reaction was complete the yellow solid was filtered off and washed with water, acetone and ether, yield 0·85 g (65%), m.p. 180° dec. (Found: C, 47·66; H, 4·37; N, 8·53. Required for $C_{13}H_6N_2O_4\ 4H_2O$: C, 47·85; H, 4·33; N, 8·59%).

(c) 7,8-*Dimethyl-phenazine*-1,2,3,4-*tetrone octahydrate* (XV). Phenazine III (1·0 g) was oxidized in the same way as the II to the tetrone, yield 0·85 g (56%), m.p. 168° dec. (Found: C, 40·69; H, 6·06; N, 7·29. Required for $C_{14}H_8N_2O_4\ 8H_2O$: C, 40·78; H, 5·87; N, 6·79%).

(d) 7-*Carboxyl-phenazine*-1,2,3,4-*tetrone pentahydrate* (XVI) prepared from V in the same way as XV, yield 59%, m.p. 130° dec. (Found: C, 41·79; H, 3·83; N, 7·25. Required for $C_{13}H_4N_2O_6\ 5H_2O$: C, 41·72; H, 3·77; N, 7·49%).

(e) 7-*Chlorophenazine*-1,2,3,4-*tetrone heptahydrate* (XVII) prepared from IV in the same way as compounds XV and XVI, yield 62%; m.p. 185° dec. (Found: C, 36·57; H, 4·23; N, 7·10. Required for $C_{12}H_3N_2O_4Cl\cdot 7H_2O$: C, 35·96; H, 4·28; N, 6·99%).

The croconic acid condensation products were prepared by the method of Eistert *et al.*[7]

(a) *Quinoxalino*[2.3-*d*]2,3-*dihydroxy-cyclopentadien*-1-*one hemihydrate* (XVIII), yield 79%; m.p. ~280° dec. (Found: C, 59·28; H, 3·44; N, 12·78. Calc. for $C_{11}H_6N_2O_3.\ \frac{1}{2}H_2O$: C, 59·19; H, 3·17; N, 12·55%).

(b) 6,7-*Dimethyl-quinoxalino*[2.3-*d*]2,3-*dihydroxy-cyclopentadien*-1-*one-hydrate* (XIX), yield 84%; m.p. >300°. (Found: C, 59·88; H, 4·67; N, 10·64. Required for $C_{13}H_{10}N_2O_3H_2O$: C, 59·99; H, 4·65; N, 10·77%).

(c) *Quinoxalino*[2.3-*d*]*cyclopentane*-1,2,3-*trione-hydrate* (XX), yield 97%; m.p. 225° dec. (Found: C, 57·28; H, 2·51; N, 12·65. Calc. for $C_{11}H_4N_2O_3H_2O$: C, 57·39; H, 2·64; N, 12·17%).

The leuconic acid condensation products were prepared as follows

(a) *Diquinoxalino*[2.3-2′.3′-*b,d*]*cyclopentadien*-1-*one* (XXI). Leuconic acid pentahydrate (1 g, 0·00435 mole) was dissolved in warm dil AcOH (25 ml, 10% v/v). *o*-Phenylenediamine (1·0 g, 0·0092 mole) was dissolved in warm dil AcOH (25 ml). The two solns were mixed and allowed to cool. The yellow green solid was filtered off and washed with water, ethanol, acetone and ether. The product was recrystallized from chloroform, yield 1·2 g (92%); m.p. >300°. (Found: C, 71·81; H, 3·16; N, 19·62. Calc. for $C_{17}H_8N_4O$: C, 71·82; H, 2·84; N, 19·71%).

(b) 6,7-6′,7′-*Tetramethyldiquinoxalino*(2.3-2′.3′-*b,d*)*cyclopentadiene*-1-*one* (XXII). This compound was

prepared from leuconic acid and 4,5-dimethyl-1,2-diaminobenzene in the same way as XXI, yield 74%; m.p. >300°. (Found: C, 73·87; H, 5·26; N, 16·22. Required for $C_{21}H_{16}N_4O$: C, 74·10; H, 4·74; N, 16·46%).

Polycondensation products

(a) *Diquinoxalino*(2.3-2′.3′-*a,c*)*phenazine* (XXIII). Triquinoyl octahydrate (1 g, 0·0032 mole) was dissolved in hot dil AcOH (25 ml, 10% w/v) and added to a soln of *o*-phenylenediamine (1·1 g, 0·010 mole) in hot dil AcOH (25 ml), and allowed to cool. The yellow-green ppt was filtered off and washed with water, ethanol and acetone. The compound was purified by dissolving in hot glacial AcOH containing a few drops conc HCl. Upon cooling green crystals were obtained which were filtered off and washed with ethanol, acetone and ether, yield 1·0 g (75%); m.p. >300°. (Found: C, 74·86; H, 3·30; N, 21·78. Calc. for $C_{24}H_{12}N_6$: C, 74·99; H, 3·14; N, 21·87%).

(b) 6,7-6′,7′-*Tetramethyldiquinoxalino*(2.3-2′.3′-*a,c*)7,8-*dimethyl-phenazine dihydrate* (XXIV). This compound was prepared in the same way as XXIII. The product was purified by dissolving in chloroform and passing down an alumina packed column. The pale green compound was eluted with chloroform and isolated by the removal of the solvent under reduced press, yield 55%; m.p. >300°. (Found: C, 71·26; H, 5·68; N, 16·83. Required for $C_{30}H_{24}N_6 \cdot 2H_2O$: C, 71·41; H, 5·59; N, 16·66%).

(c) *Quinoxalino*(2.3-a)3,4-*dihydroxyphenazine hydrate* (XXV). This was prepared from rhodizonic acid dihydrate and *o*-phenylenediamine by the method of Eistert *et al.*[7], yield 74%; m.p. 295 305° dec. (Found: C, 64·19; H, 3·66; N, 16·54. Calc. for $C_{18}H_{10}N_4O_2 \cdot H_2O$: C, 65·05; H, 3·64; N, 16·86%).

(d) *Quinoxalino*(2.3*a*)*phenazine*-3,4-*dione dihydrate* (XXVI). This was prepared by oxidizing XXV using the method of Eistert *et al.*,[7] yield quantitative; m.p. 220° dec. (Found: C, 62·27; H, 3·56; N, 16·28. Calc. for $C_{18}H_8N_4O_2 \cdot 2H_2O$: C, 62·07; H, 3·47; N, 16·09%).

The proton NMR spectra were run on a Perkin-Elmer R.10 spectrometer, and the IR spectra on a Perkin-Elmer 337E grating spectrophotometer.

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