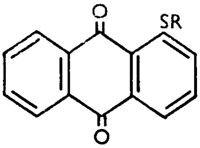
816. *Organic Sulphur Compounds. Part I. The Structure of Anthra-9 : 10-quinone-1-sulphenic Acid, its Derivatives, and Analogues.*

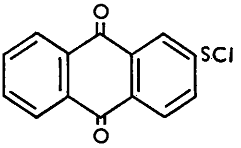
By J. A. Barltrop and K. J. Morgan.

The structures of anthra-9 : 10-quinone-1-sulphenic acid, its potassium salt, and its methyl ester are discussed. From an examination of the infrared and ultraviolet spectra of these and analogous compounds, the structure (I; R = OH) is deemed to be most probable for the acid.

Although derivatives of the sulphenic acids are well known,[1] only two such acids have been obtained as potassium salts and only one has been isolated as the free acid. Fries [2] prepared anthraquinone-1-sulphenic acid (I; R = OH) and its potassium salt, and 1-aminoanthraquinone-4-sulphenic acid has been obtained [3] as its potassium salt but not in the free state. Subsequently, many unsuccessful attempts were made [4] to synthesise other sulphenic acids. Even compounds closely analogous to anthraquinone-1-sulphenic acid appear not to be capable of isolation. Hydrolysis of anthraquinone-2-sulphenyl chloride (II) gave,[5] not the acid, but the corresponding sulphenic anhydride; similarly methyl fluorenone-1-sulphenate (III) led [6] only to a mixture of the sulphinic acid and the disulphide. However, several of the analogous selenenic acids have been synthesised.[7]



(I)



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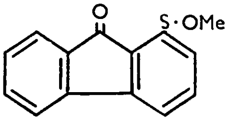

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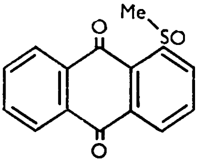

(IV)

A number of explanations of the apparently unique stability of anthraquinone-1-sulphenic acid have been advanced. Kharasch *et al.*[6, 8] suggested that the stability is due to hydrogen bonding (cf. V). Since the site of the acidic hydrogen atom has not been adequately established [2, 9] the equivalent structure (VI) has to be considered. Containing, as it does, an O • • • H–S hydrogen bond, the stability to be conferred by this structure is less [10] than that of the O • • • H–O bonded structure although some stabilisation

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[1] Rathke, *Ber.*, 1870, **3**, 858; Zincke, *Ber.*, 1911, **44**, 769.

[2] Fries, *Ber.*, 1912, **45**, 2965.

[3] Fries and Schürmann, *Ber.*, 1919, **52**, 2182.

[4] Zincke and Baeumer, *Annalen*, 1918, **416**, 86; Zincke and Eismayer, *Ber.*, 1918, **51**, 751; Zincke and Farr, *Annalen*, 1912, **391**, 57; Zincke and Lenhardt, *ibid.*, 1913, **400**, 9; Zincke and Röse, *ibid.*, 1914, **406**, 103.

[5] Fries and Schürmann, *Ber.*, 1919, **52**, 2170.

[6] Kharasch and Bruicie, *J. Amer. Chem. Soc.*, 1951, **73**, 3240.

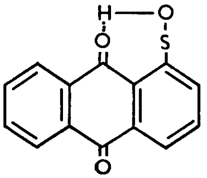
[7] Behaghel and Hofmann, *Ber.*, 1939, **72**, 582; Behaghel and Seibert, *Ber.*, 1933, **66**, 708; Behaghe and Müller, *ibid.*, 1935, **68**, 1540; 1934, **67**, 105; Jenny, *Helv. Chim. Acta*, 1952, **35**, 1429.

[8] Kharasch, Potempa, and Wehrmeister, *Chem. Rev.*, 1946, **39**, 269.

[9] Cf. Gutmann, *Ber.*, 1908, **41**, 1650.

[10] *Ann. Reports*, 1946, **43**, 153; Copley, Marvel, and Ginsberg, *J. Amer. Chem. Soc.*, 1939, **61**, 3161; Gordy and Standord, *ibid.*, 1940, **62**, 497.

might be expected from the replacement of a seven-membered chelate ring by a six-membered one. Lecher and Hardy [11] recently have suggested that the sulphenic acid is, in fact, the phenolic lactone (VII) of anthraquinol-1-sulphinic acid. The stability of a sulphinic ester may be presumed to be greater than that of a sulphenic acid; the acidity is assumed to be due to the free phenolic hydroxyl group. Such a quinol structure may be expected to equilibrate with the tautomeric oxanthrone structure (VIII) although this possibility was not considered by Lecher and Hardy, and under certain conditions the latter might well represent the sulphenic acid.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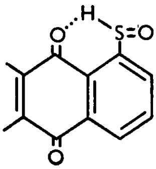
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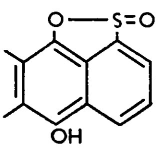
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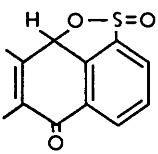
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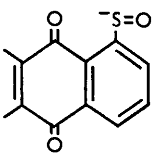
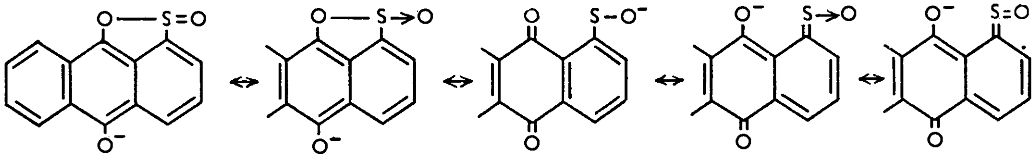
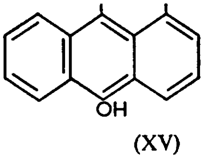

(IX)

Chemical evidence for the structure of the sulphenic acid is quite inconclusive. Reaction of the sulphenyl chloride (I; R = Cl) with methanol [2] gives the methyl ester (I; R = OMe), isomeric with, but distinct from, the methyl sulphoxide (IV). The methyl ester is readily hydrolysed by alkali to the blue-green salt of the sulphenic acid which on cautious acidification gives the red sulphenic acid. The acid reacts [2] with hydrogen chloride to give the sulphenyl chloride (I; R = Cl) and with hydrogen bromide to give the corresponding sulphenyl bromide. It may be noted that the reverse reaction, the direct hydrolysis of the acid chloride to the acid, leads to decomposition products. The free acid is methylated by methyl sulphate [2] to the ester (I; R = OMe); the alkali-metal salts treated similarly yield [2] the sulphoxide (IV). Sulphinic acids also give esters and sulphones by alkylation of, respectively, the acid and the salt.[12] This, and the colour of the salts, suggest that in the sulphenate anion a significant negative charge resides on the sulphur atom (IX) rather than on the oxygen atoms as is written by Lecher and Hardy [11] (X—XIV).


(X) (XI) (XII) (XIII) (XIV)

The structure proposed by Lecher and Hardy [11] can be applied not only to the sulphenic acid but also to certain analogous compounds. In particular, the structure of 1-mercaptoanthraquinone (I; R = H) might be written as the sulphenic lactone (XV), for in alkaline solution 1-mercaptoanthraquinone gives a blue-violet solution, whereas anthraquinone-1-sulphenic acid similarly gives a blue potassium salt. This analogy, however, may not be sound since a similar blue colour in alkaline solution is given by 2-mercaptoanthraquinone.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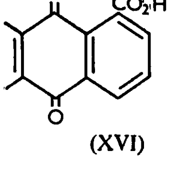
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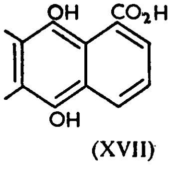
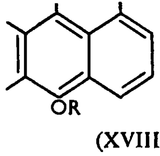
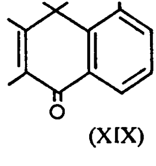

(XVII)


(XVIII)


(XIX)

A series of carboxylic acid derivatives of anthracene exists which offers more reliable structural analogies to the possible structures of anthraquinone-1-sulphenic acid.

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[11] Lecher and Hardy, *J. Org. Chem.*, 1955, **20**, 475.
[12] Rheinboldt, Mott, and Motzkus, *J. prakt. Chem.*, 1932, **134**, 257.

Specimens of these, namely, (XVI), (XVII), and (XVIII; R = H and Ac), were prepared with the intention of using them as spectral models. The free quinol (XVII) is autoxidised so rapidly that it was useless for this purpose. The lactone (XVIII; R = H) was not stable, but by rapid working it was possible to record its ultraviolet spectrum; in particular, the change red (acid) ⟶ blue (salt), similar to that of the sulphenic acid, was observed. The spectral data so obtained were compared with those obtained from the free sulphenic acid, its derivatives, and other analogous systems (Tables 1 and 2).

Infrared Spectra.—Flett [13] has examined the infrared spectra of a large number of anthracene derivatives. As might be expected, anthraquinols show no absorption in the carbonyl region but exhibit a band in the region associated with a hydrogen-bonded O–H stretching frequency (3300 cm.$^{-1}$).

Many anthraquinones show one band in the carbonyl region between 1675 and 1686 cm.$^{-1}$. The infrared spectra of anthraquinone-1-sulphenic acid, its potassium salt, and its methyl ester all show a strong band in the carbonyl region (1664—1672 cm.$^{-1}$); so also does 1-mercaptoanthraquinone (Table 1). This serves strongly to confirm that the methyl sulphenate has the anthraquinone structure (I; R = OMe). In addition, the sulphenic derivatives exhibit a peak of medium-low intensity at 1626—1634 cm.$^{-1}$, which in the case of the acid may well be due to hydrogen bonding: a twin peak at 1636 cm.$^{-1}$ is observed [13] in 1-hydroxyanthraquinone, but the occurrence of a similar band in the ester and also, weakly, in the mercapto-compound, makes its significance doubtful.

A recent analysis [14] of the spectra of aromatic sulphinic acids identifies three groups of absorption band prominent in the spectra of their esters: 1126—1136 cm.$^{-1}$ (S=O stretching), 960 cm.$^{-1}$ (S–O stretching), and a broad band near 752 cm.$^{-1}$. An absorption band at 963—960 cm.$^{-1}$ is observed in our three sulphenic compounds, another also at 1122—1136 cm.$^{-1}$. Both these bands are here considerably weaker than those reported by Detoni and Hadzi [14] and it seems that little significance can be attached to them in these circumstances. This is particularly true of the band at 1136 cm.$^{-1}$, which occurs in the approximate position of bands found in polysubstituted aromatic compounds and also of bands due to certain aromatic ketones. It may be noted that 1-mercaptoanthraquinone shows weak bands at 1139 and 952 cm.$^{-1}$.

TABLE 1. *Infrared spectra.*

Anthraquinone derivative	Medium	Band frequencies (in cm.$^{-1}$) OH	CO	Other bands		
1-Sulphenic acid	Nujol mull	3125 (w) (broad)	1672 (s)	1631 (w)	1134 (w)	962 (m)
	$CHCl_3$ (conc.)	3330—3510 (w)	1672 (s)	1634 (m)	1136 (w)	960 (m)
	$CHCl_3$ (dil.)	3510 (w)	1669 (s)	1631 (m)	1135 (m)	960 (m)
Potassium 1-sulphenate ...	Nujol mull	—	1678 (s)	—	1122 (w)	963 (m)
Methyl 1-sulphenate	Nujol mull	—	1664 (s)	1626 (m)	1130 (m)	961 (m)
1-Mercapto [a]	Nujol mull	—	1669 (s)	1639 (w)	1139 (w)	952 (w)

[a] The compound shows no SH band in the region 2600—2550 cm.$^{-1}$.

The variation of the position and form of the band corresponding to the O–H stretching vibration in the sulphenic acid is of interest. Appearing as a broad band of low intensity at about 3125 cm.$^{-1}$ in the solid state, it occurs in solution as a sharp, but still weak band at 3509 cm.$^{-1}$. It seems that this is due to a polymeric association through intermolecular hydrogen bonds which on dissolution and dilution break and re-form to give a singly bridged intramolecular hydrogen bond, C=O · · · H–O. The former is known [15a] to give rise to broad-banded absorption in the region 3200—3450 cm.$^{-1}$. If, as is argued below, the sulphenic acid is best represented as R·S·OH, any intramolecular hydrogen bonding (V) could not be chelate-conjugated and would be expected [15b] to show a sharp band between 3450 and 3570 cm.$^{-1}$. [The alternative structure (VI) should not show O–H bands.] Anthraquinol exhibits [13] a broad band at 3300 cm.$^{-1}$.

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[13] Flett, *J.*, 1948, 1441.

[14] Detoni and Hadzi, *J.*, 1955, 3163.

[15] (*a*) Bellamy, " Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1954, p. 88; (*b*) *op. cit.*, p. 89.

TABLE 2. *Ultraviolet absorption spectra.*

Anthraquinone derivative	λ (mμ)	ε	λ (mμ) *	ε	λ (mμ)	ε	λ (mμ)	ε	λ (mμ)	ε	λ (mμ)	ε	λ (mμ)	ε	λ (mμ)	ε
1-Carboxylic acid	251	36,000	[272]	12,600	—	—	329	4700	—	—	—	—	—	—	—	—
Potassium 1-carboxylate	250	38,000	[272]	13,000	—	—	335	4100	—	—	—	—	—	—	—	—
Methyl carboxylate	254	45,000	[270]	19,600	[305]	4140	324	4700	—	—	—	—	—	—	—	—
1-Sulphinic acid	256	31,000	[273]	10,000	—	—	328	3900	—	—	—	—	—	—	—	—
Methyl 1-sulphoxide	250	—	[270]	—	[300]	—	320	—	—	—	—	—	—	—	—	—
1-Mercapto-	251	30,200	[270]	12,000	[300]	3200	[315]	2900	—	—	—	—	—	—	—	—
Potassium 1-mercaptide	249	35,700	[270]	14,000	[300]	4000	315	4100	395	2100	—	—	—	—	—	—
1-Sulphenic acid	248	43,200	[270]	15,800	—	—	314	5500	—	—	—	—	—	—	—	—
Potassium 1-sulphenate	250	41,000	[270]	14,800	[306]	6300	317	6200	—	—	—	—	—	—	—	—
Methyl 1-sulphenate	247	29,400	[266]	13,800	304	4900	[325]	2760	—	—	—	—	—	—	—	—
9 : 10-Diacetoxyanthracene ...	255	235,000	—	—	—	—	354	8500	372	12,800	393	11,400	—	—	—	—
Lactone acetate of 1-carboxyanthraquinol (XVIII; R = Ac)	237	23,500	262	73,400	—	—	—	—	—	—	—	—	—	—	—	—
Lactone of 1-carboxyanthraquinol (XVIII; R = H) ...	239	21,200	265	19,400	284	25,000	306	8700	340	572	368	519	488	1570	790	7600
Potassium salt (XVIII; R = K)	255	28,500	305	17,000	[340]	5700	390	3800	—	—	—	—	—	—	—	—
Anthrone	260	22,800	[293]	7400	[303]	4800	[335]	867	368	536	—	—	—	—	—	—
10-Methyloxanthrone	275	20,800	[303]	5000	—	—	—	—	—	—	—	—	—	—	—	—
Autoxidation product from 1-carboxyanthraquinol	248	34,000	[270]	13,600	305	2700	330	4800	—	—	—	—	—	—	—	—
Autoxidation product from lactone (XVIII; R = H) ...	252	27,300	[268]	12,200	316	1900	—	—	—	—	—	—	—	—	—	—

All spectra were measured on methanol solutions. Except for the lactone (XVIII; R = H), in which measurements were extended into the visible region, all spectra were measured in the range 200—400 mμ.

* Data in square brackets refer to points of inflexion.

Ultraviolet Spectra.—The ultraviolet spectra of anthraquinones have been widely studied.[16] Four bands appear to characterise the anthraquinone nucleus: two benzenoid bands at 246—257 mμ (ε 29,000—48,000) and at 312—333 mμ (ε 2900—7000), and two quinonoid bands at 261—266 mμ (ε 12,400—23,000) and at 270—277 mμ (ε 11,000—18,400). The bands at 265 mμ are frequently absent but the other three bands appear regularly in the spectra of a wide range of substituted anthraquinones; the nature of the substituent has little effect on the position of these bands. There are also bands in the visible region, the position and intensity of which vary largely with the substituent.

The data presented in Table 2 for substances of known anthraquinonoid structure (1—8) conform to this analysis. The band at 265 mμ is uniformly absent. The other absorption bands fall within the limits 247—256 mμ (ε 29,000—45,000), 266—273 mμ (ε 12,000—19,000), and 315—335 mμ (ε 2900—4700). The spectra of the sulphenic acid and its potassium salt show bands within these limits: 248, 250 mμ (ε 43,200, 41,000), 270 mμ (ε 15,800, 14,800), and 314, 317 mμ (ε 5500, 6100). These data strongly support the quinonoid structure of the sulphenic acid and its salt.

A comparison of these results with the spectral data for anthraquinols serves further to support this. The spectrum of 9 : 10-diacetoxyanthracene shows one peak of very high intensity at 255 mμ (ε 236,000). Replacement of one acetoxy-group by a five-membered lactone ring (XVIII; R = Ac) causes some reduction in intensity and a simultaneous shift in the position of the maximum absorption (262 mμ; ε 73,400). When the second acetyl group is removed to leave the free phenolic lactone (XVIII; R = H), a structure analogous to Lecher and Hardy's sulphenic acid formulation (VII),[11] the spectrum undergoes a complete change: the absorption maximum at 265 mμ is of greatly reduced intensity (ε 19,400) and there appear new maxima at 284, 306, 340, and 368 mμ, corresponding closely in position to those found for anthrone, *viz.*, 260, 293, 303, 335, and 368 mμ. (Martin [17] finds for anthrone: $\lambda_{\text{max.}}$ 260, 292, 299, 304, 349, 368 mμ.) It may be deduced from this that the equilibrium between the quinol (XVIII; R = H) and the oxanthrone (XIX) structure lies well on the side of the latter in solution in methanol. It may be noted that the positions of the absorption maxima of the lactone, here recorded, differ markedly from those reported by Scholl and Böttger,[18] *viz.*, 258 (ε 1600), 272 (ε 1600), and 351 mμ (ε 2250). Solutions of the lactone autoxidise rapidly, and after short standing a solution of the lactone (XVIII; R = H) showed absorption maxima at 252 (ε 27,300), 268 (ε 12,200), and 316 mμ (ε 1900), values which are more closely related to those of Scholl and Böttger and strongly suggest a quinonoid structure. Even more readily oxidised is the potassium salt of the lactone (XVIII; R = K), the blue solution of which is completely decolorised in a few minutes. By working rapidly, it was possible to obtain an approximate spectrum of this salt; it shows a similarity to that of the parent lactone. The free 1-carboxyanthraquinol (XVII) was too unstable to permit any measurements: its autoxidation products appear to be quinonoid.

The absorption of many of these anthracene compounds extends into the visible region; in particular, the potassium salts of anthraquinone-1-thiol, anthraquinone-1-sulphenic acid, and of the phenolic lactone (XVIII, R = K) all produce blue solutions. Although little of any general structural significance can be deduced from measurements in this region, for the positions of maxima and the values of extinction coefficients are sensitive functions of the substituent groups, yet a direct comparison of spectra can be illuminating, and it was hoped to obtain data which would enable a decision to be made between the alternative R·S·OH and R·SH:O structures for the sulphenic acid by comparing its spectrum with those of the ester (I; R = MeO) and the isomeric sulphoxide (IV). The latter was too sparingly soluble in methanol to permit direct comparison, but maxima were indicated at 250, 270, 300, and 320 mμ. However, Jenny [19] has compared the spectra of the ester and the sulphoxide in chloroform solution over the range 300—600 mμ. The

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[16] Morton and Earlam, *J.*, 1941, 159; Allen, Wilson, and Frame, *J. Org. Chem.*, 1942, **7**, 169; Spruit, *Rec. Trav. chim.*, 1949, **68**, 325; Hartman and Lorenz, *Z. Naturforsch.*, 1952, **7**, 360; Peters and Sumner, *J.*, 1953, 2101.

[17] Martin, *Ann. Combustibles liquides*, 1937, **12**, 97; Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127.

[18] Scholl and Böttger, *Ber.*, 1930, **63**, 2128.

[19] Jenny, *Helv. Chim. Acta*, 1952, **35**, 845.

ester had maxima at 311 (ε 6300) and 465 mμ (ε 6300); the sulphoxide at 349 (ε 5000) and 420 mμ (ε 800). The position of these bands and the extinction coefficient of the longer-wavelength band make it probable that the sulphenic acid, $\lambda_{max.}$ 314 mμ (ε 5530) and 470 mμ (ε 4500), has a structure corresponding to that of the ester, *i.e.*, R·S·OH. This conclusion is supported by infrared spectra.

The presence in many of these spectra of low-intensity peaks around 300—310 mμ may be noted. These occur mainly as points of inflexion over a range where the gradient of the spectral curve is small, so it is difficult to assess their position and intensity accurately; their significance is equally difficult to determine.

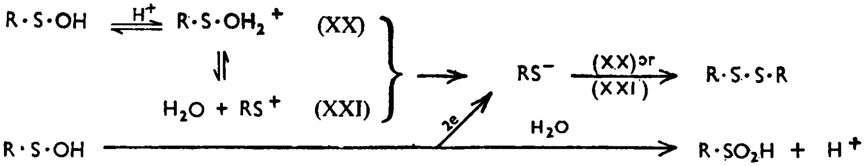
Conclusions.—Of the four structures (V)—(VIII) which have been advanced for anthra-9 : 10-quinone-1-sulphenic acid, Lecher and Hardy's formulation (VII),[11] with its tautomeric modification (VIII), can be immediately discarded, primarily because the infrared spectrum of the sulphenic acid shows the presence of a carbonyl group which is inexplicable in terms of (VII), and a hydroxyl group, which is non-existent in (VIII). In order to explain the infrared data on a tetracyclic structure, one would have to postulate that the sulphenic acid consisted of a tautomeric mixture of (VII) and (VIII), and this possibility is excluded because the ultraviolet spectrum shows a total absence of the anthrone bands which are such a prominent feature of the spectrum of the analogous carboxylic lactone (XVIII; R = H) $\rightleftharpoons$ (XIX). Furthermore, formula (VIII) can be regarded as that of an anthrone or as an oxanthrone, and Flett [13] finds that anthrones substituted in the 4-position by H, Cl, MeO, NH_2, or OH have C=O bands in the range 1645—1658 cm.$^{-1}$ (measured in the solid state) and that oxanthrones substituted in the 4-position by H, Cl, or MeO have C=O bands at about 1652 cm.$^{-1}$ (solid state). The fact that the sulphenic acid absorbs at 1672 cm.$^{-1}$ provides further evidence against the oxanthrone structure (VIII) and hence against Lecher and Hardy's formulation (VII).

We are thus led to conclude that the sulphenic acid must be an anthraquinone derivative (V) or (VI). The purely chemical evidence of its synthesis, general properties, and ease of hydrolysis, strongly suggests that the methyl anthraquinonesulphenate possesses the anthraquinone structure (I; R = MeO) and the infrared spectrum of the substance, supported by the close relation between the ultraviolet spectra of the ester and the other 1-substituted anthraquinones in Table 2, provides overwhelming support. Once this is accepted, then the obvious spectroscopic parallel between the ester and the salt and the sulphenic acid indicates that the last must also be an anthraquinone derivative. The presence of an OH group in the molecule (intramolecularly hydrogen-bonded by a single non-chelate bridge according to the infrared spectrum) then further suggests that the sulphenic acid must exist predominantly, if not exclusively, in the form (V) in dilute solution. There can be no doubt that the 1-mercaptoanthraquinone has the conventional structure (I; R = H).

It seems probable that the selenenic acids have similar structures, their superior stability being due to the reluctance of selenium to assume the higher valency states, especially in combination with oxygen.

The stability of anthraquinonesulphenic acid remains unique. Flett [13] suggests that intramolecular hydrogen bonding stabilises 1 : 4-dihydroxyanthraquinone to the extent of about 7·5 kcal. per hydroxyl group. Such stabilisation will of course be weaker in the sulphenic acids whether they contain the non-chelate O···H–O or the conjugated O···H–S bond.[10] Nevertheless, stabilisation arising from this source must be important since the only known selenenic acids [7] are those which can be stabilised by hydrogen bonding, *e.g.*, 2 : 4-dinitrobenzene-, *o*-nitrobenzene-, and 1-anthraquinone-selenenic acids, and since the non-intramolecularly bonded anthraquinone-2-sulphenic acid cannot be prepared.

This factor is insufficient by itself to explain the instability of sulphenic acids other than the 1-anthraquinonyl compound. The crux of the matter appears to be the relative resistance of anthraquinonesulphenic acid to dismutation to disulphide and sulphinic acid, the reaction apparently responsible for the spontaneous destruction of many of the other sulphenic acids. Unpublished results from this laboratory have shown that the dismutation of anthraquinone-1-sulphenic acid is acid-catalysed and may depend on the formation of the charged entity (XX or XXI) which then abstracts electrons from another molecule of the sulphenic acid :



On this view, electron-attracting groups should stabilise the sulphenic acids, by retarding the formation of (XX or XXI). However, if the substituents are too powerful, then the electron-deficient sulphur atom of the sulphenic acid itself begins to accept electrons so that dismutation can again take place. Seen in these terms, stable sulphenic acids are delicately poised systems, possessing substituents sufficiently electron-attracting to inhibit dismutation through the ions (XX or XXI), yet not so strongly attracting as to induce dismutation through the electron deficiency of the SOH grouping itself.

EXPERIMENTAL

Anthraquinonesulphenic acid, its potassium salt, and its methyl ester, anthraquinone-1-sulphinic acid and methyl anthraquinone-1-sulphoxide were prepared from 1-aminoanthraquinone and purified according to Fries.[13] Anthraquinone-1-carboxylic acid,[20] most conveniently crystallised from nitric acid, was converted into its methyl ester, in good yield, by the action of diazomethane. Anthraquinol-1-carboxylic acid,[21] its lactone,[22] and its lactone acetate [21, 22] were prepared from the anthraquinonecarboxylic acid. The dark red quinol acid was oxidised immediately on exposure to air, becoming ashy-grey. The lactone, also red, was considerably more stable, but the blue colour of solutions of its potassium salt lasted only for a few seconds unless special precautions were taken. By use of methanol from which the oxygen had been expelled by prolonged passage of a stream of oxygen-free nitrogen, the duration of the colour was extended sufficiently to enable a small number of spectroscopic observations to be made. By using a large number of solutions, each measured over a small spectral range, an approximate spectrum of the salt was obtained. The lactone acetate was stable.

Specimens of 9 : 10-diacetoxyanthracene, anthrone, and methyloxanthrone were kindly supplied by Mr. M. L. Burstall. Ultraviolet spectra were measured in solution in methanol on a Unicam spectrophotometer. Infrared spectra were determined with a Perkin-Elmer spectrophotometer by Mr. F. J. Hastings, for whose technical assistance the authors express their thanks. This investigation was conducted during the tenure by one of us (K. J. M.) of a Senior Hulme Scholarship of Brasenose College, Oxford.

DYSON PERRINS LABORATORY, SOUTH PARKS ROAD, OXFORD. [*Received, May* 16*th*, 1956.]

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[20] Ullmann and van der Schalk, *Annalen*, 1912, **388**, 199.
[21] Scholl, Böttger, and Hass, *Ber.*, 1929, **62**, 616.
[22] Scholl, Renner, and Mayer, *ibid.*, p. 1278.