NOTES.

68. *Molecular Association of Oxygen and Aromatic Substances.*

By D. F. EVANS.

FRESHLY distilled dimethylaniline quickly becomes yellow in air; a much deeper colour is produced when oxygen is bubbled through the liquid. Such coloration has previously been attributed to permanent oxidation. It has been found, however, that the colour completely disappears when the dissolved oxygen is removed by a stream of nitrogen or by evacuation. Further, various aromatic substances develop a new absorption band (usually in the ultra-violet region) when saturated with oxygen at atmospheric pressure, and this band disappears when the oxygen is removed.

The spectra were measured at room temperature on a Unicam S.P. 500 spectrophotometer. The blank cell contained the pure compound or a solution of it in a neutral solvent, and the other cell a similar sample through which a stream of oxygen had been passed for some time. The spectra were measured as quickly as possible to minimise errors caused by changes in the concentration of oxygen.

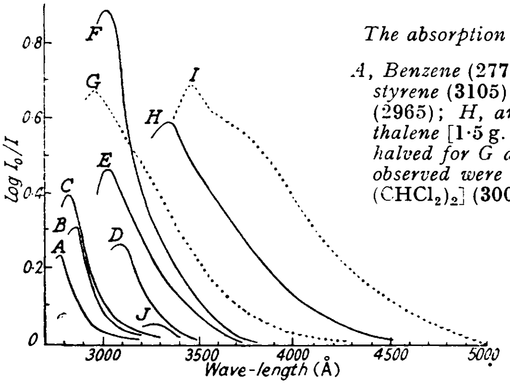
The results obtained are shown in the Figure (except three bands which are omitted to avoid overcrowding) and the positions of the maxima are given in the legend; because of the intense absorption of aromatic compounds, the latter are not very accurate, although their relative positions will not be appreciably in error. Thus, when the pure liquids were diluted with a neutral solvent, the maxima shifted to shorter wave-lengths (see Table). It was shown, for the 10% solution of anisole in tetrachloroethane, that the effect was to a large extent

Anisole solutions (by vol.)				Benzene solutions	
	$\lambda_{max.}$ (Å)		$\lambda_{max.}$ (Å)		$\lambda_{max.}$ (Å)
30% in decalin	2950	10% in Bu^{n}OH	2915	20% in *cyclo*hexane	2735
10% ,, ...	2920	10% in $(CHCl_2)_2$	2935	20% in EtOH	2735

instrumental (possibly the result of stray radiation, see below) and due to the greatly increased transparency of the solution compared with that of pure anisole, by placing as filter a cell containing a 9 : 1 mixture (by vol.) of anisole and tetrachloroethane in front of both solution and blank cells. The maximum was then obtained at about 3000 Å, *i.e.*, almost the same as for pure anisole.

The intensities of absorption shown have no quantitative significance owing to large variations in the amount of dissolved oxygen, although such differences as between benzene and pyrrole are almost certainly significant.

Oxygen dissolved in carbon tetrachloride, and also ethyl benzoate and benzaldehyde (containing *meta*-directing and electron-accepting groups), gave no appreciable absorption down to 2550, 2700, and 3100 Å respectively. With " spectroscopic " hexane and *cyclo*hexane, absorption bands starting at about 2600 Å, with apparent maxima at about 2050 Å, were obtained (optical densities about 0·6 and 1·0). These maxima, however, are almost certainly not genuine, but due to the rapid increase in scattered light at shorter wave-lengths which results in low absorption values. Spurious maxima, which were shown to be due to this effect, have been observed in a similar spectral region and on a similar instrument, by Bladon, Henbest, and Wood (*J.*, 1952, 2737) and Eglington, Jones, and Whiting (*J.*, 1952, 2873). The true maxima with hexane and *cyclo*hexane will therefore lie at wave-lengths shorter than 2050 Å.



The absorption spectra of oxygen dissolved in aromatic substances.

A, Benzene (2775); *B, chlorobenzene* (2865); *C, toluene* (2830); *D, styrene* (**3105**); *E,* m-*cresol* (**3030**); *F, anisole* (**3005**); *G, pyrrole* (2965); *H, aniline* (**3350**); *I, dimethylaniline* (**3460**); *J, naphthalene* [**1·5** g. *in* **10** c.c. *of* ($(CHCl_2)_2$] (**3270**). *Values of* log I_0/I *are halved for G and I. Figures in parentheses are* $\lambda_{max.}$ (Å). *Also observed were bromobenzene* (2885), *diphenyl* [1·5 g. *in* 10 c.c. *of* $(CHCl_2)_2$] (**3005**), *and quinol* (1·5 g. *in* 10 c.c. *of* Bu^{n}OH) (**3260**).

Since the positions of the peaks are almost unaffected by dilution of the aromatic component, it is unlikely that they are caused by an oxygen absorption band shifted by a solvent effect. More probably they are due to the formation of molecular complexes similar to those formed by aromatic substances and the halogens or sulphur dioxide (Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71,** 2703; Keefer and Andrews, *ibid.*, 1950, **72**, 4677, 7270; 1951, **73**, 462, 4169; Barb, *Proc. Roy. Soc.*, 1952, *A*, **212**, 66). These complexes give rise to absorption bands in a similar spectral region, which show a similar dependence on the nature of the aromatic substance. Thus for benzene derivatives their positions follow closely the electron-donating power of the substituent group or groups. This is particularly clearly shown in the case of oxygen, owing to the larger variety of compounds that can be studied. The nature of the halogen complexes has been discussed at length by Mulliken (*J. Amer. Chem. Soc.*, 1950, **72**, 600; 1952, **74**, 811).

It is of interest that oxygen complexes would provide a plausible initial stage in the oxidation, and especially the photo-oxidation, of aromatic substances such as phenols and amines. They may also be involved in certain cases of fluorescence quenching by oxygen.

The absorption obtained with hexane and *cyclo*hexane is unlikely to be due to the formation of complexes. It is more probable that it is due to absorption by the oxygen itself, possibly as a result of the forbidden $^3\Sigma_u{}^+ - {}^3\Sigma_g{}^-$ transition being permitted to some extent by the intermolecular forces. In gaseous oxygen this transition gives rise to a series of extremely weak absorption bands starting at about 2700 Å, with a continuum at 2425 Å (Herzberg, *Canad. J. Phys.*, 1952, **30**, 185). The increase in intensity in going from gas to solution seems very large, however. A consequence of this absorption of some practical importance is that hexane and *cyclo*hexane become considerably more transparent in the ultra-violet when deoxygenated.

Further work is in hand.

The author thanks Dr. R. E. Richards, under whose supervision this work was carried out, for help and advice, Dr. E. J. Bowen and Dr. L. E. Orgel for helpful discussions, and the Department of Scientific and Industrial Research for a Maintenance Grant.

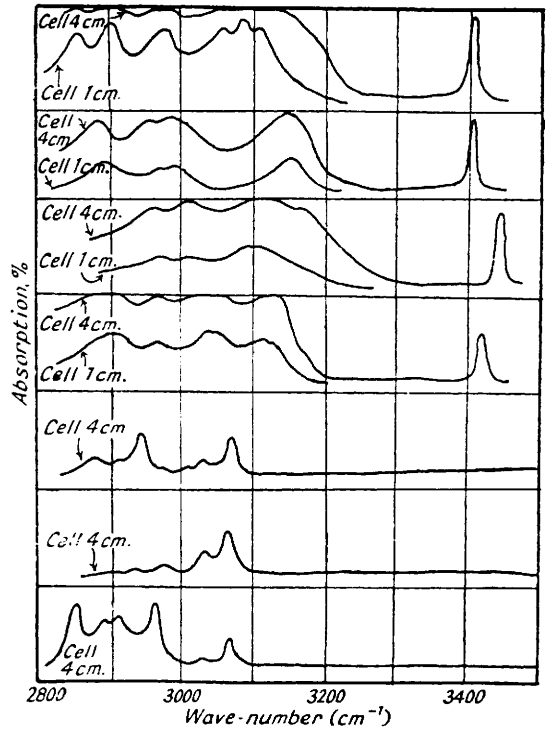
PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, August* 9*th*, 1952.]

---

69. *The Infra-red Spectra of Some Thio-amides.*

By M. ST. C. FLETT.

DURING an investigation of the vibration frequency characteristic of the C=N group, we have measured the infra-red spectra of some compounds which are commonly formulated with the group ·N:C(SH)·. Randall, Fowler, Fuson, and Dangl ("Infra-red Determination of Organic Structures," Van Nostrand, 1949) have suggested from its infra-red spectrum that in the solid state 2-mercaptothiazoline has the structure (I). Also the infra-red spectrum of 2-mercaptobenzothiazole has been reported by Mann (*Trans. Inst. Rubber Ind.*, 1951, **27**, 232) who, from the absence of an S–H band, suggests the thio-amide structure (II), but finds no band which he can associate with an NH group. Our measurements on these and related compounds in the solid state and in dilute solution in carbon tetrachloride in the 3µ region, by use of a calcium fluoride prism, throw further light on this apparent anomaly. The figure shows the spectra in this region of solutions of 2-mercaptobenzothiazole, 2-methylthiobenzothiazole, 2-mercaptobenzoxazole, 2-mercapto-4-methyl-



2-*Mercaptobenzothiazole*, 0·0072M.

2-*Mercaptothiazoline*, 0·0057M.

2-*Mercaptobenzoxazole*, 0·0043M.

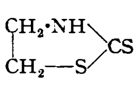
2-*Mercapto-4-methylthiazole*, 0·0050M.

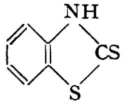
2-*Methylthiobenzothiazole*, 0·0055M.

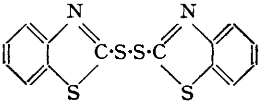
Dibenzothiazolyl disulphide, 0·0030M.

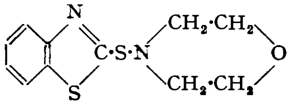
2-*Benzothiazolylsulphenomorpholide*, 0·0042M.

thiazole, 2-mercaptothiazoline, dibenzothiazolyl disulphide (III), and 2-benzothiazolylsulphenomorpholide (IV).


(I)


(II)


(III)


(IV)

There is a striking difference between the spectra of those compounds where there is a possibility of tautomerism involving ·NH·CS· and ·N:C(SH)· and those where the hydrogen atom is replaced. The former show a sharp band near 3430 cm.$^{-1}$ and very strong broad bands between 2900 and 3100 cm., whose strength makes it most unlikely that they are connected with either aromatic or aliphatic C–H links. Also, when the spectrum of 2-mercaptobenzothiazole was measured at various concentrations, the relative strengths of the sharp and broad bands varied with dilution. By analogy with the spectra of amides in solution (Richards and Thompson, *J.*, 1947, 1248), the sharp band is therefore assigned to the N–H vibration of monomers containing ·NH·CS· groups, and the broad band to modified N–H vibrations of hydrogen-bonded complexes in equilibrium with those monomers.

None of the spectra of the solids showed the sharp band near 3430 cm.$^{-1}$, but the strong absorption around 3000—3100 cm.$^{-1}$ persisted in those cases where a thio-amide structure was possible. In no case was a band near 2500 cm.$^{-1}$ found which could be associated with SH.

From these results it appears that each of the compounds 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptothiazoline, and 2-mercapto-4-methylthiazole exists in the solid state as hydrogen-bonded thio-amide complexes, which partially break down in carbon tetrachloride solution.

It is interesting that the N–H bands of the hydrogen-bonded form should be at the abnormally low wave-number of 3000—3100, and be so broad. This is in marked contrast to the behaviour of *N*-substituted amides (*idem, ibid.*) where values of 3430 cm.$^{-1}$ for the monomers and 3270 for the complexes were found. Clearly $>$N—H . . . O=C$<$ and $>$N—H . . . S=C$<$ bonds differ greatly, though it is hardly permissible to assume from the much greater frequency shift accompanying bonding in the latter case that N—H . . . S=C bonds are stronger. The spectral changes accompanying association of thio-amides resemble rather those of carboxylic acid dimerisation (Davies and Sutherland, *J. Chem. Phys.*, 1938, **6**, 755) than of amide association.

Imperial Chemical Industries Limited, Research Laboratories,
Hexagon House, Manchester, 9.

[*Received, August 26th*, 1952.]

---

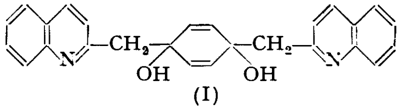
70. *The Interaction of Quinolines with Aldehydes and Ketones.*

By F. Bell.

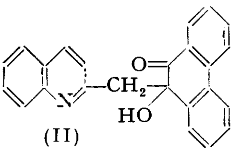
The undermentioned compounds were prepared during an examination of the use of *m*-nitrobenzaldehyde for elimination of reactive quinolines from mixtures of coal-tar bases. When a quinaldine is heated with an equal amount of *m*-nitrobenzaldehyde at 120° for 6 hours the product is usually an alcohol; only on longer heating or on crystallisation from acetic anhydride does this pass into the styrene. This is contrary to the commonly held view (see, *e.g.*, Sidgwick's "Organic Chemistry of Nitrogen," Oxford Univ. Press, 1942, p. 554). Some experiments were made on the interaction of these bases with benzoquinone, phenanthraquinone and benzil.

Experimental.—*2-2′-Hydroxy-2′-*m*-nitrophenylethyl-lepidine*, after being washed with ethanol, crystallised from benzene in prisms, m. p. 165—167° (Found: C, 70·1; H, 5·1. $C_{18}H_{16}O_3N_2$

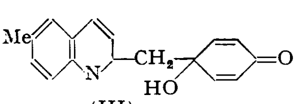
requires C, 70·1; H, 5·2%). On dissolution in boiling acetic anhydride it gave 2-*m*-nitrostyryllepidine, m. p. 186°. *2-2′-Hydroxy-2′-*m*-nitrophenylethyl-6-methylquinoline* crystallised from benzene in almost colourless prisms, m. p. 142—144° (Found: C, 70·8; H, 5·5%), and similarly gave 6-methyl-2-*m*-nitrostyrylquinoline. *3-Methyl-2-*m*-nitrostyrylquinoline* crystallised from acetic anhydride in needles, m. p. 148—150° (Found: C, 74·6; H, 5·1. $C_{18}H_{14}O_2N_2$ requires C, 74·5; H, 4·8%), and the *7-methyl* isomer formed yellow needles, m. p. 192°, from benzene or acetic anhydride (Found: C, 74·0; H, 4·7%).



(I)



(II)



(III)

Quinaldine and benzoquinone at 150° (or in boiling xylene) reacted briskly to give a black product, readily purified by recrystallisation from xylene to yield almost colourless rosettes, m. p. 154°. This *compound* appears to be (I) (Found: C, 79·9; H, 6·1; N, 7·3. $C_{26}H_{22}O_2N_2$ requires C, 79·2; H, 5·6; N, 7·1%) for on dissolution in acetic anhydride and precipitation with water it gave quinol diacetate. Quinaldine and benzil gave 2-α-benzoylstyrylquinoline, m. p. 191°, in poor yield (McElvain and Johnson, *J. Amer. Chem. Soc.*, 1941, **63**, 2213, give m. p. 187—188°).

Quinaldine and phenanthraquinone were heated at 200° (bath) for ¼ hour; cooling gave a black paste which was rubbed with ethanol, and the residue was filtered off and crystallised from benzene, yielding needles, m. p. 169°. Longer heating gave a tar from which it was not possible to isolate crystalline material. This compound (m. p. 165°) had been prepared previously by Benrath and Meyer (*J. pr. Chem.*, 1914, **89**, 266) by the long exposure of a mixture of quinaldine and phenanthraquinone to sunlight. They ascribed to it a rather improbable formula. Structure (II) appears more probable but, surprisingly, the compound crystallised unchanged from acetic anhydride. 2 : 6-Dimethylquinoline with phenanthraquinone gave an analogous *compound*, m. p. 135° (Found: N, 3·8. $C_{25}H_{19}O_2N$ requires N, 3·8%), but α-picoline, 2 : 3-lutidine, and 3 : 4-lutidine did not react under these conditions.

2 : 3-Dimethylquinoline with benzil at 150° for 1½ hours gave 2-α-benzoylstyryl-3-methylquinoline, m. p. 248°, previously described by Rohde (*Ber.*, 1934, **67**, 431).

2 : 6-Dimethylquinoline with benzoquinone gave a *compound*, which crystallised from xylene in rosettes, m. p. 137—139°, and for which structure (III) is suggested (Found: C, 76·5; H, 6·4; N, 5·4. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7; N, 5·3%).

HERIOT-WATT COLLEGE, EDINBURGH.

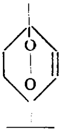
[*Received, August 28th,* 1952.]

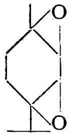
---

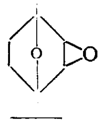
71. *Ascaridole Glycol Anhydride.*

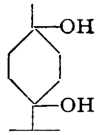
By M. MATIC and DONALD A. SUTTON.

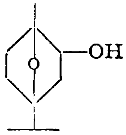
NELSON (*J. Amer. Chem. Soc.*, 1913, **35**, 84) suggested that ascaridole glycol anhydride obtained from ascaridole (I) at 150° was (II) and then probably passed into a more stable form (III) (cf. Thoms and Dobke, *Arch. Pharm.*, 1930, **268**, 128). The anhydride, prepared by isomerisation of ascaridole in boiling xylene (Henry and Paget, *J.*, 1921, **119**, 1714) and purified by vacuum-distillation, had no specific ultra-violet absorption bands and no hydroxyl groups, and appeared to be homogeneous. It was reduced by lithium aluminium hydride to a liquid mixture which was not resolved by vacuum-distillation but on counter-current solvent distribution separation yielded *ca.* 20% of *cis*-1 : 4-terpin (IV), independently of the time of heating during preparation of the anhydride. The oxiran rings in (II) thus seem established for at least part of the product. The other main reduction product had a higher partition coefficient but on evaporation of its aqueous solution yielded a trihydric alcohol, $C_{10}H_{20}O_3$, m. p. 162—163°, of lower partition coefficient. Formation of this is tentatively postulated as being due to hydration of the internal 1 : 4-ether bridge of (V) or (VI) the expected products of lithium aluminium hydride reduction of (III).

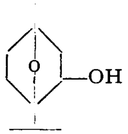

(I)


(II)


(III)


(IV)


(V)


(VI)

Hydrogenation of the anhydride in methanol at 150°/60 atm. in the presence of Raney nickel (cf. Newman *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 3362) afforded *ca.* 4% of *cis*-1 : 4-terpin together with at least two unidentified substances.

Experimental.—Ascaridole glycol anhydride. Ascaridole (77 g.) in xylene (50 c.c.) was added dropwise to boiling xylene (200 c.c.), and three such solutions were refluxed (at 650 mm.) for 6, 18, and 24 hours respectively. The isomerisation product (48 g.) (b. p. 76°/1 mm.) recovered by distillation through a column with an efficiency 15 theoretical plates (packed with Dixon rings; *J. Soc. Chem. Ind.*, 1949, **68**, 88) was easily separated from unchanged ascaridole in the forerun. The main fractions from the 6- and 18-hour preparations were split into a number of sub-fractions by distillation, but since these had almost identical refractive indices (n_D^{30} 1·4595—1·4602) they were recombined [Found : C, 71·4; H, 9·75; HO ($LiAlH_4$ method), 0. Calc. for $C_{10}H_{16}O_2$: C, 71·4; H, 9·5%].

Lithium aluminium hydride reduction. The anhydride (6-hour preparation) (3·11 g., 0·0185 mol.) and lithium aluminium hydride (0·55 g., 0·0145 mol.) in ether (2 hours' refluxing) gave a product (3·0 g.) (Found : C, 68·9; H, 11·5%) which on counter-current distribution [ethanol (20), water (30), *iso*hexane (30), and ethyl acetate (20). Craig, " Techniques of Organic Chemistry," Vol. III, 1950, Weissberger)] yielded *cis*-1 : 4-terpin, m. p. and mixed m. p. 117° (K = 0·32; 19%) (Found : C, 70·0; H, 12·0. Calc. for $C_{10}H_{20}O_2$: C, 70·0; H, 11·6%), and a solution of a substance of K 1·00 (19%). Evaporation of the latter gave a *triol*, m. p. 162—163° [Found : C, 64·1 ; H, 11·05 ; active H ($LiAlH_4$ in tetrahydrofuran), 1·45% ; M (Rast), 185, 182. $C_{10}H_{20}O_3$ requires C, 63·8; H, 10·65; 3 active H, 1·6% ; M, 188] (K 0·14).

The authors thank Mr. F. W. G. Schöning for carrying out the microanalyses. This note is published by permission of the South African Council for Scientific and Industrial Research.

South African Council for Scientific and Industrial Research,
National Chemical Research Laboratory, Pretoria.

[*Received, September 1st 1952.*]

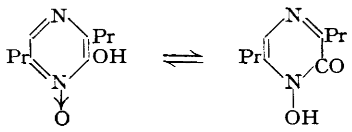
---

72. *Some 10-Substituted 1 : 3-Dimethyl-2 : 9-diazaphenanthrene 9-Oxides.*

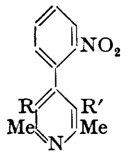
By S. B. Hansen and V. Petrow.

The hydroxamic acid group present in aspergillic acid (I) is responsible for its antibacterial action (Dutcher, *J. Biol. Chem.*, 1947, **171**, 321. Cf. 1-hydroxy-2-pyridone and -2-quinolone; Newbold and Spring, *J.*, 1948, 1864; Shaw, *J. Amer. Chem. Soc.*, 1949, **71**, 67 ; Lott and Shaw, *ibid.*, p. 70). We therefore prepared some tricyclic analogues.

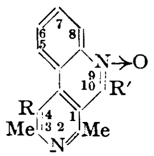
Friedländer and Ostermaier (*Ber.*, 1881, **14**, 1916; Friedländer, *ibid.*, 1914, **47**, 3369) obtained 2-hydroxyquinoline 1-oxide as a minor product of reduction of ethyl *o*-nitrocinnamate with alcoholic ammonium sulphide. We find that zinc dust and ethanol readily convert diethyl 2 : 6-dimethyl-4-*o*-nitrophenylpyridine-3 : 5-dicarboxylate (II; R = R′ = CO_2Et) into 4-carbethoxy-10-hydroxy-1 : 3-dimethyl-2 : 9-diazaphenanthrene 9-oxide (III; R = CO_2Et, R′ = OH). Similar reductions of the appropriate pyridines gave 4-cyano-10-hydroxy-1 : 3-dimethyl- (III; R = CN, R′ = OH), 4-acetyl-1 : 3 : 10-trimethyl- (III; R = Ac, R′ = Me), 10-amino-1 : 3-dimethyl- (III; R = H, R′ = NH_2), and 10-amino-4-cyano-1 : 3-dimethyl-2 : 9-diazaphenanthrene 9-oxide (III; $R = CN$; $R' = NH_2$) (cf. Bauer, *Ber.*, 1938, **71**, 2226; Sharp and Spring, *J.*, 1951, 932). These oxides gave colours with ferric chloride, the first (but not the third) gave a blue copper salt, and the last two gave reddish-brown precipitates with nickel salts. All liberated iodine from warm acidulated potassium iodide (cf. Newbold and Spring, *J.*, 1949, S 133). These reactions support their structures. In contrast to their monocyclic analogues (Spring and his co-workers, *loc. cit.*) they underwent profound decomposition on attempted acetylation.



(I)



(II)



(III)

Experimental.—M. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.

4-*Carbethoxy*-10-*hydroxy*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene* 9-*oxide* (III; $R = CO_2Et$, $R' = OH$). Diethyl 2 : 6-dimethyl-4-*o*-nitrophenylpyridine-3 : 5-dicarboxylate (1·9 g.) (Hinkel, Ayling, and Morgan, *J.*, 1931, 1837) and ammonium chloride (750 mg.) in water (40 ml.) and alcohol (20 ml.) were treated at 60° with zinc dust (60 mg.), portionwise with stirring. After a further 1 hour concentrated hydrochloric acid (0·35 ml.) was added, stirring was maintained for 1 hour, and the crystalline solids were collected. Purification from methanol yielded 4-*carbethoxy*-10-*hydroxy*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene* 9-*oxide* (75%), yellow needles, m. p. 180° (Found : C, 65·3; H, 5·0; N, 9·5. $C_{17}H_{16}O_4N_2$ requires C, 65·4; H, 5·1; N, 9·0%).

4-*Cyano*-10-*hydroxy*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene* 9-*oxide* (III; $R = CN$, $R' = OH$) was obtained (25%) from methanol in pale yellow needles, m. p. 230° (Found : C, 67·6; H, 4·0; N, 15·9. $C_{15}H_{11}O_2N_3$ requires C, 67·9; H, 4·1; N, 15·8%).

4-*Acetyl*-1 : 3 : 10-*trimethyl*-2 : 9-*diazaphenanthrene* 9-*oxide* (III; $R = Ac$; $R' = Me$), after crystallisation from methanol, formed (35%) yellow plates, m. p. 218° (Found : C, 72·4; H, 5·6; N, 10·4. $C_{17}H_{16}O_2N_2$ requires C, 72·8; H, 5·7; N, 10·0%).

4-*Cyano*-1 : 3 : 10-*trimethyl*-2 : 9-*diazaphenanthrene* 9-*oxide*, pale yellow needles, m. p. 243—244° (from benzene) (Found : C, 72·8; H, 5·0; N, 16·4. $C_{16}H_{13}ON_3$ requires C, 73·0; H, 4·9; N, 16·0%), was obtained together with some 4-*cyano*-1 : 3 : 10-*trimethyl*-2 : 9-*diazaphenanthrene*, m. p. 217—218° (from alcohol) (Found : C, 77·3; H, 5·0; N, 17·3. $C_{16}H_{13}N_3$ requires C, 77·7; H, 5·3; N, 17·0%), by reduction of (II; $R' = Ac$, $R = CN$) (Courts and Petrow, *J.*, 1952, 1) with stannous chloride in boiling hydrochloric–acetic acid.

10-*Amino*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene* 9-*oxide* (III; $R = H$, $R' = NH_2$) separated from ligroin–ethanol in yellow needles, m. p. 256—258° (decomp.) (Found : C, 69·8; H, 5·6; N, 18·1. $C_{14}H_{13}ON_3$ requires C, 70·3; H, 5·4; N, 17·6%).

10-*Amino*-4-*cyano*-1 : 3-*dimethyl*-2 : 9-*diazaphenanthrene* 9-*oxide* (III; $R = CN$, $R' = NH_2$) was obtained (30%) from methanol in yellow spangles, m. p. 250° (decomp.) (Found : C, 67·7; H, 4·5; N, 19·8. $C_{15}H_{12}ON_4$ requires C, 68·2; H, 4·5; N, 21·2%).

The authors thank the Directors of The British Drug Houses Ltd. for permission to publish these results.

RESEARCH LABORATORIES, THE BRITISH DRUG HOUSES, LTD.,
LONDON, N.1.

[*Received, September* 11*th*, 1952.]

73. *Influence of Temperature on the Spectrum of 9 : 10-Diphenylanthracene.*

By J. C. D. Brand and J. R. Davidson.

The colour of a solution of 9 : 10-diphenylanthracene is intensified by heat. This property was first attributed (Ingold and Marshall, *J.*, 1926, 3080; Schlenk and Bergmann, *Annalen*, 1928, **463**, 179; Schönberg, Ismail, and Asker, *J.*, 1946, 442) to the co-existence in equilibrium of a coloured biradical form of higher energy, but chemical evidence cited in support of this has been shown to be inadmissible (Barnett, Cook, and Wiltshire, *J.*, 1927, 1724) and it is now also known that the lowest triplet level of anthracene * is far too high to be thermally populated (Reid, *J. Chem. Physics*, 1952, **20**, 1214; Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100); however, the spectroscopic explanation of the colour change has not been satisfactorily determined. From a qualitative spectral examination Dufraisse and Houpillart (*Bull. Soc. chim.*, 1938, **5**, 1628) suggested that the yellow colour arose owing to the proximity of the ultra-violet absorption system to the visible region; with rise in temperature, according to these authors, there is a general increase in intensity of absorption which causes the low-frequency tail of the ultra-violet band to spread into the visible region, leading to a temperature-dependent yellow colour. From the fact that no *new* absorption band appeared Dufraisse *et al.* concluded that the equilibrium postulated by Ingold and Marshall did not exist, but this inference was not entirely justified because, if it were correct that the intensity of the ultra-violet bands is temperature-dependent, there must be an equilibrium between two states of different energy to account for it.

The spectra of anthracene and 9 : 10-diphenylanthracene, at 18° and 100°, are shown in the Figure. Contrary to the earlier suggestion, the integrated intensity of absorption ($\int \varepsilon d\bar{\nu}$) of 9 : 10-diphenylanthracene is *independent* of temperature, and this excludes the possibility that the yellow colour is associated with an equilibrium between two molecular states with different zero-point energies. Between 18° and 100° the only spectral change is due to the normal Franck–Condon broadening of the ultra-violet absorption, *i.e.*, to the change of transition probability resulting from the variation with temperature of the distribution of molecules over the vibrational levels of the ground state. With rising temperature, this effect leads to an increment of intensity where ε is small and a decrement where ε is large (Gibson, Rice, and Bayliss, *Phys. Review*, 1933, **44**, 193; Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419); these changes are recorded in the $\Delta\varepsilon$ curve in the Figure where it can be seen that the maxima in the vibrational envelope, including partially resolved maxima, correspond to minima in $\Delta\varepsilon$. With 9 : 10-diphenylanthracene the broadening on the low-frequency side of the first maximum (3950 Å) causes an increase of absorption in the visible region, the colour sensation at 100°, relative to 18°, being equivalent to that produced by a band having $\varepsilon_{\text{max.}}$ ~130 at 4150 Å. The shape of the "difference" band in this region is shown on an enlarged scale in the Figure. The effect with anthracene is very similar but, with the loss of the phenyl substituents, the spectrum is displaced by about 1200 cm.$^{-1}$ to higher frequencies and the changes occur just outside the visible limit. One can understand, therefore, why thermochromism in anthracene derivatives occurs with bathochromic substituents other than phenyl (*e.g.*, with alkyl; Barnett, Cook, and Wiltshire, *loc. cit.*) and why groups such as *p*-methoxyphenyl and *p*-chlorophenyl, which are more powerfully bathochromic than phenyl, produce a greater depth of visible colour.

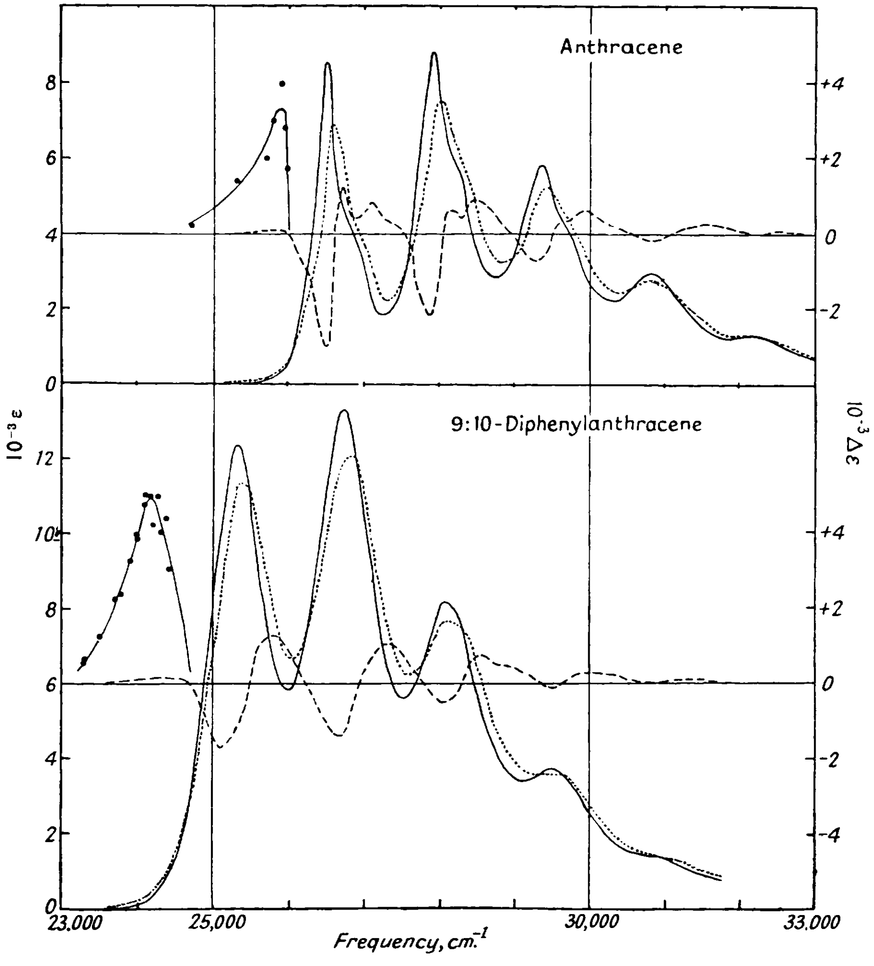
Experimental.—9 : 10-Diphenylanthracene, prepared by the method of Dufraisse and Le Bras (*Bull. Soc. chim.*, 1937, **4**, 1037), had m. p. 248·5° (uncorr.).

---

* 9 : 10-Diphenylanthracene should resemble anthracene closely in this respect, as in the singlet spectrum, because of the restriction on co-planarity (Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127).

Spectra. Extinction coefficients were measured with a Unicam SP 500 Spectrophotometer, fitted with a small electronically controlled thermostatic cell-compartment regulated to ±0·3°. Water or glycol was used as bath-liquid. The wave-length calibration of the monochromator was slightly affected by conduction of heat from the thermostat and the calibration was referred to the Hg arc spectrum at both temperatures; the maximum difference observed with the bath at 100° was about 10 Å. The measurements refer to solutions in decalin, and the extinction coefficients at 100° are corrected for expansion of the solvent (data of Grubb and Kistiakowsky, *loc. cit.*). No permanent change in the spectrum due to heating was detected when the solution was re-examined at room temperature (Table).

Spectra of anthracene and 9 : 10-*diphenylanthracene in decalin* (*temp.* 18° *and* 100°).



——— ε, 18°; - - - - - ε, 100°; — — — Δε; —●—●— Δε × 40.

	$f = 4{\cdot}31 \times 10^{-9}\int\varepsilon d\bar{\nu}$ at 18°	$f = 4{\cdot}31 \times 10^{-9}\int\varepsilon d\bar{\nu}$ at 100°	Limits of integration (cm.$^{-1}$)
Anthracene	0·099	0·098	25,000—33,500
9 : 10-Diphenylanthracene	0·173	0·175	23,000—31,500

A A

Variation of ε *with temperature* (*low-frequency region*).

λ, Å (uncorr.)	$(\text{cm. mole l.}^{-1})^{-1}$				$(\text{cm. mole l.}^{-1})^{-1}$			
	ε_{18}	ε_{100}	ε_{18}	$\Delta\varepsilon$ *	ε_{18}	ε_{100}	ε_{18}	$\Delta\varepsilon$ *
	9 : 10-*Diphenylanthracene.*							
	Expt. 1				Expt. 2			
4250	—	59	13	+34	16	59	13	+33
4200	44	142	52	+60	47	133	50	+63
4150	198	410	214	+122	201	411	198	+119
4100	881	1,265	911	+110	873	1,275	885	+110
4050	3,237	3,480	3,252	−280	3,175	3,409	3,195	−240
4000	8,130	7,760	8,180	−1060	8,110	7,570	7,760	−1450
3970	—	—	—	—	11,380	10,080	11,400	−1600
3950	12,370	11,260	12,450	−1400	12,390	11,320	12,390	−1120
3930	—	—	—	—	11,700	11,120	11,550	−360
3900	8.210	8,840	8,110	+740	8,200	8,860	8,150	+1100
3850	5,880	6,730	5,860	+920	5,850	6,670	5,850	+940
3800	8,470	8,650	8,540	−500	8,480	8,470	8,480	−380
	Anthracene.							
4000	8	34	8	+23				
3950	16	51	16	+32				
3900	47	104	43	+53				
3850	428	600	460	0				
3800	4020	3269	4230	−1700				
3770	8410	6948	8380	−2600				
3750	5308	5802	5160	+1000				
3730	4081	4280	4090	+460				
3700	2840	3234	2762	+580				
3680	1855	2332	1855	+650				

* The figures in this column are corrected for change of wave-length calibration with temperature. Values of ε_{100}, however, are uncorrected and in general, therefore, $\Delta\varepsilon$ is not equal to the difference between col. 3 and the average of cols. 2 and 4.

Grants in support of this work from the Chemical Society and from D.S.I.R. are gratefully acknowledged.

THE UNIVERSITY, GLASGOW, W.2.

[*Received, September* 20*th*, 1952.]

---

74. *The Chlorostannates of Dimethyl Ketazine and Certain Hydrazones.*

By W. PUGH and A. M. STEPHEN.

WE recently (*J.*, 1952, 4138) described the preparation of compounds containing the hydrazinium and chlorostannate ions together with some aliphatic ketones, in which, pending crystal structural examination, the ketones were represented merely as solvent of crystallisation. Anomalies which appeared in the analysis of similarly prepared compounds of antimony and bismuth, to be reported later, have led us to re-examine the composition of these substances, to discard the 2 : 4-dinitrophenylhydrazine method of ketone estimation (Iddles and Jackson, *Ind. Eng. Chem.*, *Anal.*, 1934, **6**, 454; Houghton, *Amer. J. Pharm.*, 1934, **106**, 62; Perkins and Edwards, *ibid.*, 1935, **107**, 208), and to apply the hypoiodite method (Messinger, *Ber.*, 1888, **21**, 3366; Goodwin, *J. Amer. Chem. Soc.*, 1920, **42**, 39; Cassar, *Ind. Eng. Chem.*, 1927, **19**, 1061) to the compounds with acetone and ethyl methyl ketone. Much higher values have thereby been obtained, necessitating the formulation of these compounds as chlorostannates of dimethyl ketazine and butanone hydrazone respectively. Combustion analysis confirms the new formulation. These substances are completely hydrolysed in acid solution, yielding hydrazinium ions and free ketone in the ion-mol. ratio 1 : 2 for the ketazine compound and 1 : 1 for butanone hydrazone. Correspondingly, the compounds with diethyl ketone and di-*n*-propyl ketone are to be formulated as chlorostannates of pentan-3-one hydrazone and heptan-4-one hydrazone.

Dimethyl ketazine has been shown to be completely decomposed in acid solution to a mixture of hydrazine salt (1 mol.) and acetone (2 mols.). Its basic character, difficult to demonstrate for this reason and because of its acid-lability (Frey and Hoffmann, *Monatsh.*, 1901, **22**, 760), and certainly unexpected in view of Gilbert's observation (*J. Amer. Chem. Soc.*, 1929, **51**, 3402) that it has no basic function in aqueous acetone, is now established by the preparation of its chlorostannate from aqueous acetone. In the presence of a small excess of hydrochloric acid, on the other hand, dimethyl ketazine and stannic chloride in acetone solution deposit slowly the isomeric chlorostannate of 3 : 5 : 5-trimethylpyrazoline, with 2 mols. of acetone as determined by Messinger's method (*loc. cit.*).

Experimental.—Samples of the compounds previously reported were either recrystallised or made afresh. Nitrogen was estimated as hydrazine (by the Dumas method in the pyrazolinium salt), and acetone and ethyl methyl ketone were determined by Messinger's method after distillation of the ketone from dilute acid solution.

Bis(dimethyl ketazinium) chlorostannate forms clear rhombs, m. p. 137—138° [Found : C, 26·1; H, 4·5; N, 10·0; Sn, 21·1; Cl', 38·0; C_3H_6O, 42·2. $(C_6H_{13}N_2)_2SnCl_6$ requires C, 25·8; H, 4·66; N, 10·0; Sn, 21·3; Cl', 38·2; C_3H_6O, 41·4%].

Bis(butanone hydrazonium) chlorostannate separates as tetragonal prisms, m. p. 90° [Found : C, 19·1; H, 4·4; N, 11·1; Sn, 23·3; Cl', 42·1; C_4H_8O, 28·0. $(C_4H_{11}N_2)_2SnCl_6$ requires C, 19·0; H, 4·35; N, 11·1; Sn, 23·5; Cl', 42·1; C_4H_8O, 28·5%].

Bis(pentan-3-one hydrazonium) chlorostannate forms rectangular prisms, m. p. 157° [Found : C, 21·4; H, 4·7; N, 10·6; Sn, 22·5; Cl', 39·8. $(C_5H_{13}N_2)_2SnCl_6$ requires C, 22·5; H, 4·9; N, 10·5; Sn, 22·3; Cl', 39·9%]. This compound and that described immediately below are very sensitive to atmospheric moisture; they smell strongly of ketone, which probably accounts for the low values for carbon and hydrogen.

Bis(heptan-4-one hydrazonium) chlorostannate separates as clear rhombs, m. p. 87—89° [Found : C, 28·2; H, 5·7; N, 9·45; Sn, 20·3; Cl', 36·5. $(C_7H_{17}N_2)_2SnCl_6$ requires C, 28·5; H, 5·8; N, 9·5; Sn, 20·1; Cl', 36·1%].

Addition of stannic chloride (0·6 c.c.) to a solution of dimethylketazine (0·8 c.c.) in light petroleum (b. p. 80—100°; freshly distilled over Na) gave a white solid. Mixing this with concentrated hydrochloric acid (0·5 c.c.) in excess of acetone–ether and allowing the solvents to evaporate caused deposition of *bis*-3 : 5 : *5-trimethylpyrazolinium chlorostannate* (with acetone of crystallisation), m. p. and mixed m. p. 218—219° [Found, in material dried at 80° *in vacuo* : Sn, 17·6; Cl', 32·0; C_3H_6O, 18·0. $(C_6H_{13}N_2)_2SnCl_6,2C_3H_6O$ requires Sn, 17·7; Cl', 31·6; C_3H_6O, 17·2%].

We are indebted to Mr. R. von Holdt and Mr. M. C. B. Hotz for carrying out some of the analyses.

UNIVERSITY OF CAPE TOWN. [*Received, October 13th*, 1952.]

---

75. *Eudesmic Acid : Its Identity with* 3 : 4 : 5-*Trimethoxybenzoic Acid.*

By A. J. BIRCH and (MRS.) P. ELLIOTT.

EUDESMIC ACID, m. p. 168°, was identified as its amyl ester in the oil of *Eucalyptus aggregata* by Smith (*J. Proc. Roy. Soc. N.S.W.*, 1900, **34**, 72). He assigned to it the formula $C_{14}H_{18}O_2$ (mol. wt. 218) (cf. Baker and Smith, " A Research on the Eucalypts," Sydney, 1920, p. 404), apparently on the basis of analyses of the silver salt (Found : Ag, 33·9, 33·3. Calc. for $C_{14}H_{17}O_2Ag$: Ag, 33·2%) and the " dibromide," m. p. 102—103° (Found : Br, 41·75. Calc. for $C_{14}H_{18}O_2Br_2$: Br, 42·6%). Smith converted the acid by hot nitric acid into an acid, m. p. 113°, considered to be probably cumic acid. He thought that eudesmic acid was an alkylcinnamic acid. About 30 mg. of Smith's specimen were available in the University collection and have now been proved to be 3 : 4 : 5-trimethoxybenzoic acid.

Several occurrences of this acid in Nature have been recorded, *e.g.*, in *Prunus virginiana* (Power and Moore, *J.*, 1909, **95**, 253), and its relation to gallic acid is obvious.

Experimental.—The eudesmic acid, which was probably more than fifty years old, had m. p. 164°, raised to 168° by crystallisation from water (Found: C, 57·0; H, 6·0. Calc. for $C_{10}H_{12}O_5$: C, 56·6; H, 5·7%), and undepressed by an authentic specimen of 3 : 4 : 5-trimethoxybenzoic acid obtained by the methylation of gallic acid. The methyl ester was prepared in refluxing methanolic sulphuric acid (10%) (1 hour), and crystallised from aqueous methanol as needles, m. p. 79°. Smith's analyses agree with this formulation (Calc. for $C_{10}H_{11}O_5Ag$: Ag, 33·8. Calc. for $C_{10}H_{10}O_5Br_2$: Br, 43·3%). The ultra-violet absorption ($\lambda_{max.}$ 262 mμ, ε 9970, in EtOH) indicates a carboxyl group attached directly to a benzene ring. The oxidation product was perhaps impure 1 : 2 : 3-trimethoxy-4 : 5-dinitrobenzoic acid (m. p. 126°), known to be thus formed from the trimethoxybenzoic acid (Will, *Ber.*, 1888, **21**, 612).

UNIVERSITY OF SYDNEY, N.S.W.

[*Received, October* 20*th*, 1952.]