146. *Fading and Tendering Activity in Anthraquinonoid Vat Dyes. Part I. Electronic Absorption Spectra of Dye Solutions.*

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The absorption spectra of 39 anthraquinonoid vat dyes and related quinones have been determined in ethanol solution (ultraviolet and visible spectra) and in chlorobenzene (visible spectra); the visible spectra of the corresponding *leuco*-derivatives in aqueous solution have also been measured. The spectra of most of the compounds are interpreted in terms of the quasi-classical Lewis–Calvin model, together with the electromeric properties of substituent groups and additional fused rings. The two bands exhibited by most of the *leuco*-derivatives are regarded as derived from the x and y bands of the corresponding quinones by considerable bathochromic displacement due to the ionic charges on the phenolic oxygen atoms. For most of the dyes the ethanol spectra are displaced bathochromically from the chlorobenzene spectra, indicating some dye–ethanol association. Although there is no simple relation between spectra and fading–tendering activity, weak absorption bands, attributed to singlet–triplet transitions, are exhibited by most active, but not by any inactive, dyes. Many of the dyes exhibit marked fluorescence, which may be related to photo-activity, and which is shown to cause deviations from Beer's and Lambert's laws.

It is well known that certain vat dyes, mainly anthraquinonoid yellow, orange, red, and some brown, but rarely blue, violet, or green dyes, when exposed to light as dyeings on cellulose substrates, are active in the sense of themselves fading, or causing preferential

fading of an accompanying inactive dye, or causing accelerated tendering (oxidative degradation) of the substrate in the presence of air, strong alkali, sodium hypochlorite, hydrogen peroxide, or alkaline reductants which convert the dyes into the *leuco*-form; the *leuco*-dyes also cause tendering in the dark during re-oxidation. Previous work has been adequately reviewed.[1-3] The present work is an attempt to resolve the part played by light absorption by the dye in the fading and tendering processes. In this paper are reported the ultraviolet and visible absorption spectra of solutions of several active and inactive anthraquinonoid vat dyes and related compounds, and the visible spectra of their *leuco*-derivatives. Approximate absorption and reflectance spectra for some active dyes have been given by Landolt,[4] and visible and ultraviolet absorption spectra of amino- and acylamino-anthraquinones have been discussed by Peters and Sumner.[5]

Apart from the observations that dyes containing a pyridine ring [6] or an NH-containing ring [7,8] are usually inactive, and that activity increases with decrease in basicity,[7] there appears to be little relation between molecular structure and activity for vat dyes. In fact, other types of dye,[9,10] and even ferrous hydroxide,[11] zinc oxide and sulphide, and titania [12] exhibit tendering activity. Scholefield and Turner [1] quote Preston's observation that only the active vat dyes absorb in the 3600—4000 Å region. Luszczak and Zukriegel [13] attempted to correlate the light fastness (L) (arbitrary scale, range 0—14) of dyes with the wavelength (λ, in Å) of the ultraviolet absorption maximum, by means of the empirical equation $L = 14 - 10800/(4000 - \lambda)$. This is unsatisfactory for vat dyes since, apart from omitting consideration of visible-light absorption, it predicts large changes in L for small changes in λ when the latter is near 4000 Å, contrary to fact. Lanigan [14] has shown that visible light will convert cellulose into oxycellulose in the presence of dye and oxygen, although in the absence of dye ultraviolet light is required; in the absence of both dye and oxygen, ultraviolet light degrades cellulose to a form capable of subsequent reaction with oxygen [15] in the dark.

Experimental and Results

Purification of Dyes.—Samples were received as batch pastes or fine powders containing unspecified dispersing agents and diluents. After preliminary steam distillation in alkaline suspension for some specimens, the filtered paste or powder was dissolved in the minimum quantity of concentrated sulphuric acid, and the solution diluted slowly with water, whilst being well cooled to avoid hydrolysis of acylamino- or other groups, until the original dye colour was just perceptible. On vigorous stirring of the solution, the dye was completely reprecipitated. The finely-divided precipitate was filtered off, washed free from acid with water, rinsed with acetone, and dried *in vacuo* at 60°. The product was recrystallised from a saturated solution in chlorobenzene obtained by continuous Soxhlet extraction; periodically, as extraction became too slow because of removal of the finer particles, the dye in the extraction thimble was removed, dried, finely ground, and replaced for further extraction. The recrystallised product was filtered off and dried in an air current at *ca.* 40°. The progress of purification was checked by absorption spectroscopic and microscopic examination at each stage; only for Caledon Gold Orange G and Indanthren Brilliant Orange 4RN did recrystallisation markedly affect the

[1] Scholefield and Turner, *J. Text. Inst.*, 1933, **24**, P131.
[2] Waly, Preston, Scholefield, and Turner, *J. Soc. Dyers and Col.*, 1945, **61**, 245.
[3] Turner, *ibid.*, 1947, **63**, 362.
[4] Landolt, *J. Text. Inst.*, 1951, **42**, A563.
[5] Peters and Sumner, *J.*, 1953, 2101.
[6] Kunz, *Annuaire de l'École Supérieure de Chimie de Mulhouse*, 1933, 167.
[7] Landolt, *J. Soc. Dyers and Col.*, 1949, **65**, 659.
[8] Fox, *ibid.*, p. 508.
[9] Clibbens and Little, *J. Text. Inst.*, 1946, **37**, T219.
[10] Egerton, *J. Soc. Dyers and Col.*, 1948, **64**, 336.
[11] Nabar and Turner, *ibid.*, 1945, **61**, 258.
[12] Egerton, *ibid.*, 1949, **65**, 764.
[13] Luszczak and Zukriegel, *Melliand Textilber.*, 1951, **32**, 868.
[14] Lanigan, *J. Text. Inst.*, 1948, **39**, T285.
[15] Stillings and Van Nostrand, *J. Amer. Chem. Soc.*, 1944, **66**, 753.

absorption spectra. Active dyes, if dried in contact with filter paper, or extracted in cellulose Soxhlet thimbles, underwent decomposition and disintegrated the cellulose; this was avoided by using sintered-glass apparatus.

FIG. 1. *Cibanone Golden Yellow GK in ethanol* *A*, 1·8 × 10^{-5}M; *B*, 3·6 × 10^{-5}M.

FIG. 2. *Cibanone Orange R in ethanol*: *A*, 4·4 × 10^{-4}M; *B*, 1·4 × 10^{-3}M (*double optical-density scale values*).

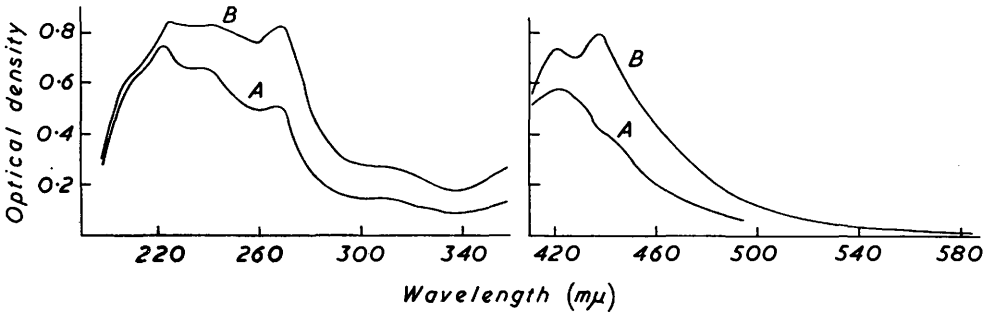
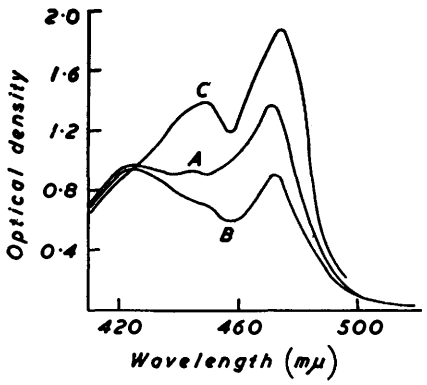


FIG. 3. *Cibanone Golden Yellow RK in chlorobenzene*: *A*, 2·6 × 10^{-4}M; *B*, 1·3 × 10^{-4}M; *C*, 5·2 × $10M^{-5}$.



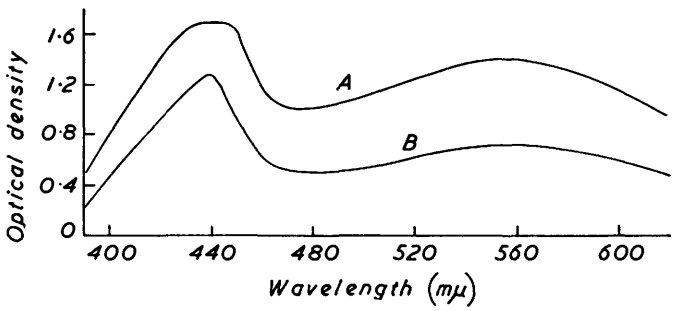


FIG. 4. leuco-*Caledon Yellow 4G in water*: *A*, 1·9 × 10^{-4}M; *B*, 3·8 × 10^{-4}M.

Other Materials.—Anthraquinone (commercial) was resublimed. Aminoanthraquinones were obtained by hydrolysing the corresponding benzoylated dyes with boiling 70% sulphuric acid for 1—2 hr., and were recrystallised from ethanol. Absolute ethanol and chlorobenzene were redistilled.

Dye Solutions.—For ultraviolet spectra, approx. 10^{-5}M-solutions in ethanol, and, for visible spectra, approx. 3 × 10^{-4}M-solutions in ethanol and in chlorobenzene were prepared by dilution of saturated solutions obtained by refluxing excess of pure dye with 100 ml. of solvent after rejection of two previous 50-ml. extracts; the concentration of the final filtered extract was determined by weighing the residue left on evaporating 50 ml. to dryness. *leuco*-Dye solutions (approx. 2 × 10^{-4}M) were prepared by treating known weights of dyes with 1% sodium dithionite solution in 0·05N-aqueous sodium hydroxide.

Absorption Spectra.—Readings were taken at intervals of 25 Å (5 Å near peaks) with the

TABLE 1. *Absorption spectra of dye solutions.*

Results are given in the form, $\lambda_{max.}$ (mμ)/log ε for (*A*) dye in ethanol, (*B*) dye in chlorobenzene, and (*C*) leuco-form in water. Italics indicate an inflection, an asterisk a plateau. Concentration *c* is in 10^{-4}M. Cell length *l* is 2 cm. unless otherwise indicated.

Anthraquinone	(*A*) *c* = 0·14 : *246/4·51*, 252·5/4·58, 263/4·22, 272·5/4·16, 325·5/3·70; *c* = 16 : 405/1·70 (*B*) *c* = 18 : 404/1·75 (*C*) *c* = 1·5 : 430/3·26, 508/3·10
1-Aminoanthraquinone	(*A*) *c* = 0·16 : 234/4·52, 276·5/4·11, *306/3·82*; *c* = 4 : *406/2·10*, *478/2·81*, 497/2·83 (*B*) *c* = 3·8 : 485/2·81 (*C*) *c* = 4 : 435/3·01, 495/2·83
1 : 4-Diaminoanthraquinone	(*A*) *c* = 0·18 : *228/4·36*, *238/4·41*, 249/4·45, *255/4·42*, *266/4·23*, *288/4·09*, 300/4·08; *c* = 2·4 : 408/1·57, *522/2·83*, 551/3·04, 592·5/3·04 (*B*) *c* = 1·9 : *516/2·90*, 545/3·04, 580/2·99 (*C*) *c* = 1·5 : 439/3·44, ~*460/3·39*
1 : 5-Diaminoanthraquinone	(*A*) *c* = 0·18 : *226·5/4·34*, 234·5/4·41, *239·5/4·36*, 277·5/4·10, *298/3·75*, *322·5/3·22*; *c* = 2·4 : *410/2·57*, *440/2·98*, 492/3·27 (*B*) *c* = 2·1 : 471/3·23, 480/3·24, *495/3·19* (*C*) *c* = 1·5 : *415/3·29*, *432/3·44*, 550/3·32
1 : 4 : 5-Triaminoanthraquinone	(*A*) *c* = 0·20 : 237/4·33, *260/3·81*, 290/3·64; *c* = 2·0 : ~*410/2·14*, *535/3·18*, 564/3·31, ~*590/3·29* (*B*) *c* = 2·2 : *428/2·26*, ~*525/3·03*, 555/3·16, *585/3·10* (*C*) *c* = 1·5 : *405/3·34*, 440/3·48, *455/3·43*, *490/3·23*
Algol Yellow WG (1-Benzamidoanthraquinone)	(*A*) *c* = 0·16 : *221/4·41*, 231·5/4·44, *274/4·47*, 282/4·49, *296/4·36*; *c* = 4·0 : 408/2·69,* 430·5/2·80 (*B*) *c* = 3·4 : 450/2·86, *460/2·84*, *470/2·77*, *485/2·65* (*C*) *c* = 1·6 : 436/3·39, *410/3·18*, 542/3·27
Caledon Red 5G (1 : 4-Dibenzamidoanthraquinone)	(*A*) *c* = 0·16 : *224/4·28*, 234/4·33, *245/4·38*, 253/4·44, 276/4·04, *356/3·34*; *c* = 2·4 : *415/2·47*, *477/2·95*, *513/3·12*, 538/3·21, *570/3·10* (*B*) *c* = 3·3 : *426/2·40*, *505/3·00*, 532·5/3·02, *570/2·86* (*C*) *c* = 1·5 : *422/3·33*, 441/3·42, 541/3·30
Caledon Yellow 3G *or* Cibanone Yellow GK (1 : 5-Dibenzamidoanthraquinone)	(*A*) *c* = 0·14 : *224/4·39*, 231/3·44, *236/4·40*, 258/4·07, *274/3·97*, *281/3·93*, 371/3·59; *c* = 2·1 : 407/3·13, 425/3·25, 465/3·21, *496/3·19* (*B*) *c* = 3·6 : *405/2·90*, 435/3·06, 452/3·06, 470/3·06, *515/2·83* (*C*) *c* = 1·5 : 430/3·33, 532/3·14, *563/3·02*
Caledon Red X5BS (1 : 4 : 5-Tribenzamidoanthraquinone)	(*A*) *c* = 0·18 : 235/4·41, 240·5/4·41, *262/4·19*, 286/4·16, *296/4·11*, *355/3·29*; *c* = 1·8 : 406/2·22, *491/2·98*, 538/3·17, *570/3·05* *590/2·92* (*B*) *c* = 2·0 : *430/2·54*, *530/3·07*, 552/3·11, *574/3·05* · (*C*) *c* = 1·5 : 441/3·40, 551/3·29
Caledon Yellow 5GK (V*a*)	(*A*) *c* = 0·20 : 227/4·25, *242/4·31*, 251/4·39, *265/4·32*, *278/4·25*, *298/3·97*; *c* = 2·0 : *410/3·19*, 426/3·27, *435/3·24* (*B*) *c* = 2·4 : *417/3·24*, 422/3·26, *439/3·19* (*C*) *c* = 1·5 : 422/3·49, 550/3·19
Caledon Yellow 4G (V*b*)	(*A*) *c* = 0·18 : *225/4·26*, 235/4·36, *239/4·32*, *249/4·23*, *256/4·16*, *265/4·12*, 272/4·08, *280/4·04*, *298/3·79*; *c* = 1·8 : 403/3·07, *427/3·08*, *469/3·19*, 490/3·22 (*B*) *c* = 2·4 : *402/2·97*, *421/3·05*, *442/3·11*, 467·5/3·16, *495/3·02* (*C*) *c* = 1·5 : 440/3·51, 553/3·27
Indanthren Yellow FFRK (VI*a*)	(*A*) *c* = 0·16 : *237/4·38*, 252/4·45, *270/4·19*, *307/3·83*, 324/3·93, 408/3·79,* 438/3·89 (*B*) *c* = 0·14 : 411/4·04, 456/3·76 (*C*) *c* = 1·5 : 435/3·52
Hydrolysate of Caledon Olive 1R (VI*b*)	(*A*) *c* = 0·14 : 237/4·44,* 247/4·46, 303/3·97; *c* = 2·1 : 406/2·42, *524/3·17*, 552/3·24, 592/3·19 (*B*) *c* = 2·4 : *410/2·43*, *490/2·92*, 546·5/3·11, *580/3·01* (*C*) *c* = 1·5 : 422/3·47, *472/3·42*, *502/3·33*
Hydrolysate of Caledon Gold Orange 3G (VI*c*)	(*A*) *c* = 0·16 : 237/4·44, 277·5/4·08; *c* = 1·6 : *408/2·88*, *465/3·19*, 490/3·24, *504/3·21* (*B*) *c* = 1·7 : *467/3·04*, 482·5/3·07, *518/3·00* (*C*) *c* = 1·5 : *402/3·36*, 415/3·45, 490·5/3·30
Caledon Olive 1R *or* Cibanone Olive 2R (VI*d*)	(*A*) *c* = 0·19 : 230/4·37, *250/4·16*, *295/3·90*, 317/3·54; *c* = 3·8; *418/2·50*, *469/2·88*, 505/3·00, *568/2·94* (*B*) *c* = 0·2 : *470/2·95*, 520/3·00, *561/2·97* (*C*) *c* = 1·5 : *425/3·17*, 465/3·26, 485/3·20, *538/3·06*
Caledon Gold Orange 3G (VI*e*)	(*A*) *c* = 0·16 : 232/4·35, *250/4·04*, 292/3·66; *c* = 3·2 : *440/2·93*, 464/3·05, 493/3·04, *532/2·52* (*B*) *c* = 2·4 : *432/2·87*, 473·5/3·13, *486/3·09*, *540/2·57* (*C*) *c* = 1·5 : *433/3·27*, *463/3·35*, 477·5/3·42, *545/2·72*
Cibanone Yellow 3R *or* Indanthren Yellow 3RT (VII)	(*A*) *c* = 0·78 : 240/4·75, 293/4·28, *329/3·58*; *c* = 3·9 : *408/3·22*, 421/3·26, 440/3·24 (*B*) *c* = 2·4 : 412/2·79, 460/2·65 (*C*) *c* = 1·5 : *425/3·17*, *494/3·36*, 515/3·37
Cibanone Yellow 2GR (VIII*a*)	(*A*) *c* = 0·26 : *240/4·13*, 250/4·17, *265/4·07*, 284/4·04, 300/4·06, *315/3·92*; *c* = 2·6 : 427·5/3·12, *445/3·03* (*B*) *c* = 2·4 : *410/2·85*, 422/2·90 (*C*) *c* = 1·5 : 432/3·48, 500/3·17, *522/3·14*
Cibanone Red G (VIII*b*)	(*A*) *c* = 0·26 : 242/4·18, *248/4·16*, *270/3·90*, *300/3·59*; *c* = 2·6 : *435/2·96*, 473/3·11, *498/3·08*, *520/3·01* (*B*) *c* = 2·4 : *438/2·85*, *468/2·96*, 486/2·98 (*C*) *c* = 1·5 : *416/3·45*, 465/3·37 *

TABLE 1. (*Continued*)

Cibanone Red 4B (VIII*c*)	(*A*) $c = 0{\cdot}22$: *238/4·13*, 250/4·18, *258/4·17*, *276/4·04*, *316/3·73*; $c = 4{\cdot}4$: *415/2·36*, 485/2·66, *542/2·55* (*B*) $c = 3{\cdot}4$: 432·5/2·41, 514/2·77, *555/2·64* (*C*) $c = 1{\cdot}5$: *412/3·27*, 433/3·37, 537/3·17
Cibanone Brilliant Orange GK (IX*a*)	(*A*) $c = 0{\cdot}18$; 230/4·40, 251·5/4·41, 285/3·92,* *365/3·48*; $c = 1{\cdot}8$: *468/2·62*, 515/2·77, 528/2·77 (*B*) $c = 4{\cdot}8$: *435/2·74*, *469/2·98*, 487·5/3·02 (*C*) $c = 1{\cdot}5$: 410/2·64, 464/3·13, 493/3·31, 572/3·38
Cibanone Brilliant Orange RK *or* Caledon Brilliant Orange 6R (IX*b*)	(*A*) $c = 0{\cdot}22$: 230·5/4·31, 255·5/4·32, 290/3·87,* *375/3·40*; $c = 2{\cdot}2$: 480/2·53, 520/2·75, 533/2·76 (*B*) $c = 4{\cdot}8$: *442/2·51*, 471/2·80, 498/2·90 (*C*) $c = 1{\cdot}5$: *396/2·37*, 493/3·44, *550/3·39*, 573/3·42
Cibanone Golden Yellow GK (X*a*)	(*A*) $c = 0{\cdot}18$: *234/4·26*, 241·5/4·33, 255/4·26,* 287/4·15, 320/3·62, *386/3·73*, *415/4·01*, 435/3·87, 465/4·06 (*B*) $c = 0{\cdot}44$: 411/3·62, 438/3·90, 466/3·98 (*C*) $c = 0{\cdot}30$: *455/3·99*, 478/4·19, *513/3·88*, 552·5/3·82
Cibanone Golden Yellow RK (X*b*)	(*A*) $c = 0{\cdot}20$: 237/4·22, 252/4·26, 290/4·09, *324/3·86*, *409/4·00*, 415/4·08, 435/4·03, 464/3·95 (*B*) $c = 0{\cdot}62$: *424/3·46*, 443/3·53, 473/3·83 (*C*) $c = 0{\cdot}30$: ~*460/4·00*, 485/4·19, *525/3·95*, *555/3·86*
Caledon Gold Orange G (XII*a*)	(*A*) $c = 0{\cdot}21$: *228/3·96*, 256/4·27, *272/4·05*, 325/3·90, 418/4·08, 432/4·09, *482/4·03* (*B*) $c = 0{\cdot}23$: *428/3·75*, 445/3·87, 474/4·09, 535/3·45,* 573/3·54 (*C*) $c = 0{\cdot}30$: ~*510/3·94*, 543/4·04, *615/3·45*
Caledon Orange 2RTS *or* Cibanone Gold Orange 2R (XII*b*)	(*A*) $c = 0{\cdot}26$: 236·5/4·18, 254/4·34, *278/3·99*, *325/3·59*, *405/3·73*, *426/3·85*, 441/3·93, *450/3·89*, *475/4·07*, 479/4·08 (*B*) $c = 0{\cdot}28$: *434·5/3·70*, 454/3·75, 484/3·95 (*C*) $c = 0{\cdot}30$: ~385/3·54, *519/3·88*, 554/4·12
Caledon Brilliant Orange 4RN (XII*c*)	(*A*) $c = 0{\cdot}17$: 224/4·25, *260/4·20*, 264/4·27, *284/3·62*, *424/3·85*, 450/3·96, 476/4·15, 550/3·58 (*B*) $c = 0{\cdot}36$: 438/3·71, 467/3·83, 498/4·10 (*C*) $c = 0{\cdot}30$: 536/4·15
Caledon Dark Blue 2R (XIII*a*)	(*A*) $c = 0{\cdot}22$: *229/4·10*, 245/4·18, *255/4·13*, *295/3·63*, 310/3·59, 362/3·53, 444/4·21, 556/2·83 (*B*) $c = 0{\cdot}28$: *404/4·02*, 423/4·15, 443/4·17, 507/3·18, 564/3·27 (*C*) $c = 0{\cdot}15$: 412/3·82, *448/3·85*, 515·5/4·38, *530/4·37*, 582/4·24
Caledon Jade Green XN (XIII*b*)	(*A*) $c = 0{\cdot}078$: *234/4·25*, 255/4·49, 296/3·85, 350/3·71, *370/3·68*; $l = 4$ cm. : 416/4·08, *482/3·62*, *538/4·10*, ~610/4·45,* *660/4·11* (*B*) $c = 0{\cdot}32$: 465/4·05, 613/4·15, *655/4·11* (*C*) $c = 0{\cdot}30$: 467/3·61, *565/4·06*, 627/4·22
Caledon Brilliant Purple 4RN (XIV)	(*A*) $c = 0{\cdot}06$: 234·5/4·82, *252/4·75*, 308/4·32, 365/4·18 *; $c = 0{\cdot}3$: 422/4·06, 570/2·81 (*B*) $c = 0{\cdot}26$: 408/3·40, *505/3·47*, 540/3·88, 582/4·09 (*C*) $c = 0{\cdot}30$: 430/3·40,* *575/4·11*, 605/4·15, 643/4·17
Caledon Blue RN *or* Cibanone Blue RSN (XV*a*)	(*A*) $c = 0{\cdot}014$: 216/4·98, *247·5/4·91*, 255/4·92, 292·5/5·17, 371/4·21; $l = 4$ cm. : 442/4·25, 482/4·25, *554/4·02*, 598/4·33, 635/4·25 (*B*) $c = 0{\cdot}026$, $l = 4$ cm. : 440/4·10, 468/4·12, 529/3·89, 624/4·18 (*C*) $c = 0{\cdot}15$: 406/4·16, *418/4·14*, 502/4·18, 528/4·15,* 690/4·21
Caledon Blue RC (XV*b*)	(*A*) $c = 0{\cdot}026$: 226/5·03, 235/5·06, 256/5·03, 287/4·99, 305/4·96; $l = 4$ cm. : 420/4·54, 609/4·46, 668/4·49 (*B*) $c = 0{\cdot}25$: 411/4·15, *430/4·11*, 485/3·94, 540/3·64, 593/3·73 (*C*) $c = 0{\cdot}15$: 420/4·38, 520/4·47, *623/4·35*, 684/4·42
Caledon Yellow GN (XVI)	(*A*) $c = 0{\cdot}21$: 239/4·36, *250/4·24*, 294/3·72, *318/3·57*, 440/3·89, *470/3·69* (*B*) $c = 0{\cdot}52$: 423/3·66, 466/3·51, 521/3·27 (*C*) $c = 0{\cdot}15$: 407/3·82, 548/4·29, 598·5/4·50, 638/4·44
Caledon Yellow 5G (XVII)	(*A*) $c = 0{\cdot}06$: 225/4·73, *231/4·70*, 252/4·64, 291·5/4·67, 400/4·26 (*B*) $c = 0{\cdot}44$: 423·5/3·88 (*C*) $c = 0{\cdot}30$: 416/4·15, 470/4·12
Cibanone Orange R (XVIII)	(*A*) $c = 0{\cdot}44$: 256/3·90, *274/3·58*, ~*295/3·22*, *328/3·17*; $c = 4{\cdot}4$: 422/2·82, *437/2·68* (*B*) $c = 5{\cdot}2$: 437/2·75, 472/2·52, *498/1·76* (*C*) $c = 1{\cdot}5$: 470/3·47
Cibanone Red 2B (XIX)	(*A*) $c = 1{\cdot}8$: 235·5/3·34, *256/2·76*, 294/2·82, 307/2·77; $c = 7{\cdot}2$: *408/2·20*, 448/2·39 (*B*) $c = 6{\cdot}8$: *438/2·26*, 461/2·32, *495/2·15*, 532/2·10 (*C*) $c = 1{\cdot}5$: 403/3·02, 648/3·40, 682/3·50
Cibanone Red RK (XX)	(*A*) $c = 2{\cdot}1$: *217/3·08*, 232/3·23, *250/3·10*, *287/2·80*, *307/2·63*; $c = 4{\cdot}2$: *424/2·88*, 451·5/2·99, *541/2·27* (*B*) $c = 1{\cdot}8$: 410/2·86, 500/3·13, 520/3·14 (*C*) $c = 1{\cdot}5$: *414/2·90*, 521/3·37
Cibanone Red FBB (XXI)	(*A*) $c = 0{\cdot}83$: 237/3·46, 283/3·22, *322/2·96*, *350/2·62*; $c = 8{\cdot}3$: *418/2·46*, 429/2·50, ~450/2·48 * (*B*) $c = 9{\cdot}8$: 435/2·51, 449/2·50, 465/2·48, 477/2·49, *489/2·44* (*C*) $c = 3{\cdot}0$: 457/3·07, *480/3·01*, 554/2·89
Indanthren Brilliant Orange GR (XXII)	(*A*) $c = 6{\cdot}2$: *230/2·73*, 241/2·81, 293/2·51, *329/1·91*, *374/1·97*, 440/2·53, 486/2·50, 544/2·57, *603/2·36* (*B*) $c = 7{\cdot}0$: *440/2·33*, 464·5/2·57, *482/2·55*, *548/2·20*, *601/1·78* (*C*) $c = 1{\cdot}5$: 431·5/3·23, 454·5/3·37. *520/2·70*, 560/2·78, 604/2·82

Hilger Uvispek spectrophotometer at room temperature (*ca.* 18°). Wavelength-drum readings were checked against the hydrogen emission spectrum and the absorption spectra of benzene and a standard didymium glass filter. The optical density scale was checked [16] against the molar extinctions of potassium nitrate at 3020 Å and potassium chromate at 3730 and 2725 Å.

Results.—Table 1 gives the wavelengths λ (mμ) and molar extinction coefficients ε of the chief absorption maxima of 39 dyes and related compounds in ethanol (ultraviolet and visible regions) and of their *leuco*-derivatives in water (visible region). Visible spectra of the dyes in chlorobenzene were also determined, in order to detect solvent effects, *e.g.*, solvent–solute association in ethanol.

Concentrations are specified in addition to log ε values, since in many cases the spectra exhibit anomalous variations in appearance with rise of concentration. Two main types of concentration effect may be distinguished. First, there is occasional solute dimerisation or association, which gives new absorption peaks and a change of colour at high concentrations, as *e.g.* with Cibanone Brilliant Orange GK and RK in ethanol. Secondly, and far more generally for the compounds investigated, absorption at certain wavelengths is followed by fluorescence emission at longer wavelengths; by using a spectrophotometer such as the Hilger Uvispek, in which there is no monochromatisation after absorption, this leads to spuriously low ε values and departures from Beer's and Lambert's laws at the absorption wavelengths concerned.[17] The overall result of this fluorescence effect is to cause changes in the relative heights of different absorption peaks, but not usually in their wavelengths, with variation in concentration. Some examples in Figs. 1—4 show that the effect is exhibited in both the visible and the ultraviolet regions, in various solvents, and by unreduced and reduced dyes. For *leuco*-Caledon Yellow 5GK, in the concentration range 4·4—0·55 × 10^{-4}M, the intensity of the 550 mμ peak obeyed Beer's law approximately, but the intensity of the 422 mμ peak decreased slowly at first upon dilution, and then far more rapidly. This behaviour occurred in aqueous ethanol over the range 0—70% ethanol, and is thus unlikely to be due to a solvent effect. The failure of Beer's law for the shorter wavelength band was found to be general for the *leuco*-derivatives.

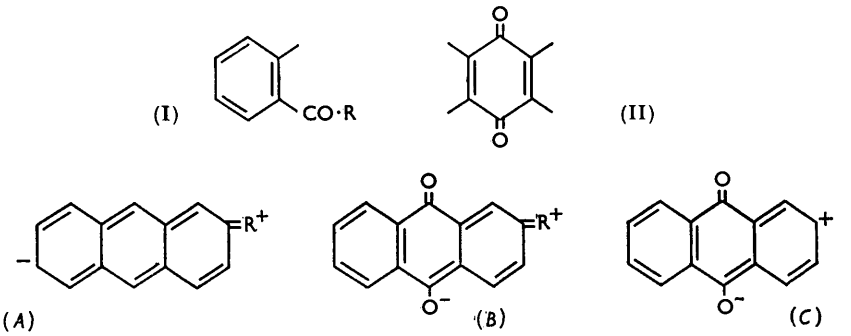
Discussion

Anthraquinone.—This is a natural reference standard for the anthraquinonoid dyes. The present spectra in ethanol agree well with earlier work,[18,19] despite variations in apparatus and solvent; however, because of the fluorescence effect, ε for the peaks at 262, 272·5, and 325·5 mμ grows far more rapidly with increasing concentration than for the 246 and 252·5 mμ peaks. Morton and Earlham [18] ascribed the 246, 252·5, and 325·5 mμ bands to the partial chromophore (I), and the weaker bands at 263, 272·5, and 405 mμ to the quinonoid chromophore (II). We prefer, following the views of Lewis and Calvin,[20] to associate the 325·5 and 252·5 mμ bands with absorption in which the electric vector of the light oscillates along the x (long) and y (short) axes of the molecule, respectively, while subsidiary peaks at 246, 263, and 272·5 mμ are ascribed to the vibrational structure of these two bands; the 272·5 mμ band might, however, be due to a weak quinonoid chromophore. The 405 mμ band, which is responsible for the pale yellow colour of anthraquinone, has a low intensity, which leads us to assign it to a singlet–triplet transition, probably within a carbonyl group.

Anthracene exhibits bands at 253 and 375 mμ. Jones [21] found that electron-donating $C_{(2)}$-substituents shifted the 253 mμ band bathochromically, owing to participation of structure (*A*), but only slightly shifted the 375 mμ band hypsochromically. He thus assigned the longer-wavelength band to an oscillation polarised along the shorter (y) molecular axis, contrary to the Lewis–Calvin view.[20] This assignment was also obtained by Coulson [22a]

[16] Lothian, " Absorption Spectrophotometry," Hilger and Watts, London, 1949, p. 176.
[17] Braude, Fawcett, and Timmons, *J.*, 1950, 1019.
[18] Morton and Earlham, *J.*, 1941, 157.
[19] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," Chapman and Hall, London, 1951.
[20] Lewis and Calvin, *Chem. Rev.*, 1939, **25**, 273.
[21] Jones, *ibid.*, 1947, **41**, 353.
[22] (*a*) Coulson, *Proc. Phys. Soc.*, 1948, *A*, **60**, 257; (*b*) Baldock, *ibid.*, 1950, *A*, **63**, 585; (*c*) Craig and Hobbins, *J.*, 1955, 539, 2309.

from L.C.A.O. molecular-orbital calculations, and despite the contrary view of Baldock,[22b] was conclusively confirmed by the work of Craig and Hobbins [22c] on the polarised spectrum of anthracene crystals. Now Peters and Sumner [5] find that electron-donating $C_{(2)}$-substituents in anthraquinone shift the 325·5 mμ band bathochromically and the 252·5 mμ band hypsochromically, owing to participation of structure (*B*). By Jones's reasoning, this supports our assignment of these bands. Further, the introduction into anthracene of the



two anthraquinonoid carbonyl groups, with opposed electron-attracting tendencies, should greatly hinder oscillations in the *y* direction, but facilitate those in the *x* direction, owing to participation of structure (*C*). Thus, the *x* and *y* band wavelengths should be much greater and smaller, respectively, for anthraquinone than for anthracene, as we have assumed.

Amino- and Acylamino-anthraquinones.—Our results for 1-aminoanthraquinone, which agree reasonably with those of Peters and Sumner,[5] may be interpreted in terms of considerable resonance contribution from dipolar structure (III) which is supported by infrared spectral evidence of weakened C=O bond strength [23] and other evidence of hydrogen bonding.[5] Participation of structure (III) lowers the excitation energy in the *x* direction, causing a bathochromic shift of the *x* band from 325·5 mμ for anthraquinone to visible wavelengths 478 and 497 mμ responsible for the red colour of the 1-amino-derivative. The *y* band is shifted hypsochromically from 252·5 to 234 mμ, in accordance with Burawoy's rules,[24] since the amino-group is only in a side chain with respect to the quinonoid ring absorption system concerned. The weaker 276·5 mμ band may correspond to the anthraquinone 272·5 mμ peak, or may be due to absorption across the amino-substituted ring. The inflection at 406 mμ corresponds to the anthraquinone 405 mμ peak. The spectrum of 1 : 4-diaminoanthraquinone may be similarly interpreted in terms of an important contribution from structure (IV), which contains a new quinonoid ring. The second amino-group has only a slight bathochromic effect on the *y* peak, which shifts from 234 to 249 mμ, although its intensity is decreased by participation of structure (IV). The *x* band, however, undergoes a large bathochromic shift (497 to 551 and 592·5 mμ) comparable with that due to the first substituent group, and caused by the increased mobility and density of the conjugation–electron system. Further, the *x* band splits into two equally intense peaks, the equality persisting on dilution. This effect, observed with several 1 : 4-disubstituted anthraquinones,[25] and associated with the new quinonoid ring in structure (IV), suggests the possibility of excitation to a new orbital with a node cutting the *x* axis; it is of interest in view of the known effect of 1 : 4-dibenzamido-substitution in decreasing fading and tendering activity.

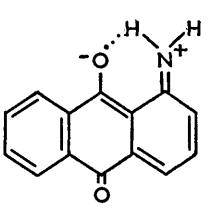
The striking spectral similarity of 1 : 5-diaminoanthraquinone and 1-aminoanthraquinone is explained by the structural similarity of the compounds and the impossibility of

[23] Flett, *J.*, 1948, 1441.
[24] Burawoy, *J.*, 1939, 1177.
[25] Wilson and Frame, *J. Org. Chem.*, 1942, **7**, 169.

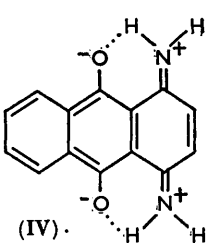
conjugation between the 1- and the 5-amino-group. The spectrum of 1 : 4 : 5-triaminoanthraquinone is practically the mean of those of the 1 : 4- and the 1 : 5-diamino-compound, indicating lack of interaction between the 4- and the 5-substituent.

In Algol Yellow WG (1-benzamidoanthraquinone), the benzoyl group reduces the electron-repellency of the amino-group and lessens the electron mobility required for resonance involving structure (III). Consequently the x transition becomes of higher energy and lower probability; the resulting lightening of colour is a well-known effect of acylation in dye chemistry. By contrast, the ultraviolet spectrum is very similar to that of 1-aminoanthraquinone. The spectra of Caledon Red 5G, Caledon Yellow 3G (= Cibanone Yellow GK), and Caledon Red X5BS (1 : 4-di-, 1 : 5-di-, and 1 : 4 : 5-tribenzamidoanthraquinone, respectively) may be similarly correlated with those of the corresponding unbenzoylated analogues. In Caledon Yellow 5GK (Va), the terephthaloyl group acts as a "chromophore insulator," [5] preventing direct conjugation of the two anthraquinone groups. The spectrum is thus like that of Algol Yellow WG, apart from additional complexity in the ultraviolet region, mainly due to a band at 251 mμ, tentatively ascribed to a benzenoid transition in the terephthaloyl group. The same band appears in the spectrum of Caledon Yellow 4G (Vb), which is otherwise similar to that of Caledon Yellow 3G.

A characteristic fearure of this group of compounds is the weak band near 400 mμ. This is probably due to a singlet–triplet transition,[26] and since its wavelength alters little on substitution, it is assumed to occur along the y axis, probably in the quinone ring. A similar band at 435 mμ occurs in the spectrum of *p*-benzoquinone.[27]



(III)



(IV)

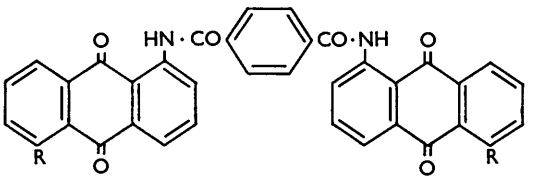
The visible spectra of this group of compounds in chlorobenzene exhibit a general hypsochromic shift as compared with the spectra in ethanol, indicating some solute–ethanol association.

The *leuco*-derivatives in alkaline solution generally exhibit two bands in the visible region, which in several cases investigated [27,28] are polarised in mutually perpendicular planes; when adsorbed on highly oriented Fortisan fibre, *leuco*-benzamidoanthraquinones are strongly dichroic in the visible region.[27] The suggestion is thus too strong to be ignored, that the two bands of the *leuco*-derivatives are essentially the x and y bands of the unreduced compounds, both displaced bathochromically owing to the lowering of transition energies caused by the presence of the ionic charges on the phenolic oxygen atoms; the y band suffers the greater shift, from the ultraviolet to the visible region, since the ionic charges greatly increase electron mobility in the y direction, but cause only smaller effects in the x direction. A similar bathochromic shift of the benzenoid band in various phenols and quinols causes the well-known colour deepening on ionisation. This interpretation of the visible spectra of *leuco*-compounds is supported by measurements, made by Mr. C. J. Cooper in this laboratory, of the ultraviolet spectra of *leuco*-solutions of anthraquinone and Caledon Red 5GS. The ultraviolet y bands of the unreduced compounds disappear on

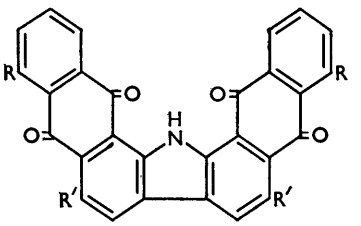
[26] Lewis, Lipkin, and Magel, *J. Amer. Chem. Soc.*, 1941, **63**, 3005; Lewis and Kasha, *ibid*, 1944, **66**, 2100; 1945, **67**, 994; Lewis and Calvin, *ibid.*, p. 1232; Kasha, *Chem. Rev.*, 1947, **41**, 401.
[27] Waters, *J. Soc. Dyers and Col.*, 1950, **66**, 544.
[28] Waters, Sumner, and Vickerstaff, *ibid.*, 1953, **69**, 181.

reduction, and new bands appear at 270 mμ (anthraquinol) and 274 and 325 mμ (*leuco*-Caledon Red 5GS), which are probably bathochromically displaced from the vacuum ultraviolet region (λ <200 mμ).

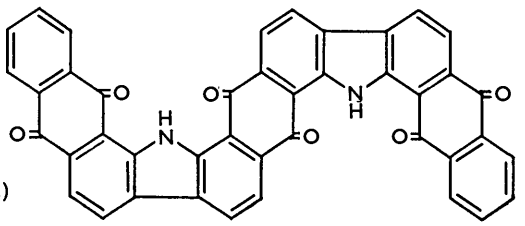
Carbazole Dyes.—The spectra of these compounds in ethanol strongly resemble those of analogues in the previous group. Thus, Indanthren Yellow FFRK (VIa) is comparable with anthraquinone. This suggests that the electromeric effect of the imino-group and its hydrogen-bonding to carbonyl groups are inhibited by the 5-membered carbazole ring, which also apparently insulates the two anthraquinone groups against mutual conjugation. The yellow colour of this dye is due to the weak 408 mμ band, which, like the 405 mμ band of anthraquinone, is ascribed to a singlet–triplet transition. The 237 mμ band may be due to absorption in the carbazole ring or, less probably, a slight 1-aminoanthraquinone character of the molecule.



(V): a ; R = H b ; R = NHBz



(VI): a ; R = R′ = H
b ; R = H, R′ = NH_2
c ; R = NH_2, R′ = H
d ; R = H, R′ = NHBz
e ; R = NHBz, R′ = H



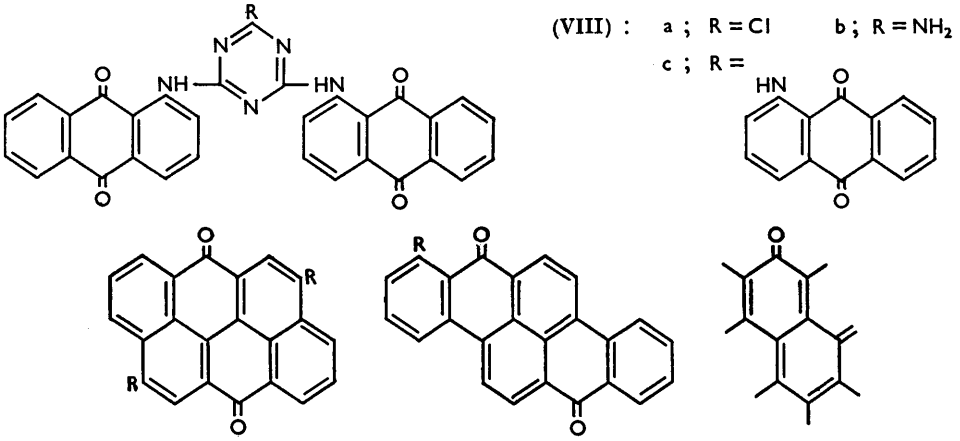
(VII)

The hydrolysates (VIb and c) of Caledon Olive 1R and Caledon Gold Orange 3G have spectra resembling those of 1 : 4- and 1 : 5-diaminoanthraquinone respectively, peak wavelengths agreeing to within about 5 mμ. Thus the ring nitrogen atom has a more pronounced amino-character here. The corresponding benzoylated dyes Caledon Olive 1R (VId) and Caledon Gold Orange 3G (VIe) have similar ultraviolet spectra which differ very little from those of their hydrolysates, apart from slightly lower intensity; thus there is little resemblance to the ultraviolet spectra of 1-mono-, or 1 : 4- or 1 : 5-di-benzamidoanthraquinones. The 230 mμ band is assigned to absorption across a quinonoid ring, as in Algol Yellow WG, and the 250 mμ band to a benzenoid transition in a benzoyl group. In the visible region, both dyes exhibit the expected strong hypsochromic effect of benzoylation, and the relation between their respective peak absorption wavelengths resembles that for 1 : 4- and 1 : 5-dibenzamidoanthraquinone. Both dyes have a weak band in the 420 mμ region. In Cibanone Yellow 3R (VII), the effect of the increased lateral extension of the molecule on the *x* band is offset by the insulating effect of the carbazole groups, resulting in only a slight bathochromic shift in the visible (*x*) bands as compared with Indanthren Yellow FFRK. In the ultraviolet region, the resemblance to the hydrolysate of Caledon Gold Orange 3G indicates some 1 : 5-diaminoanthraquinone character.

For this group of compounds, solvent effects and the relation of spectra of *leuco*-compounds to those of dyes are similar to those for the (acyl)aminoanthraquinone group.

Triazine Dyes.—In Cibanone Yellow 2GR (VIIIa), Red G (VIIIb), and Red 4B (VIIIc), the iminoanthraquinone groups are in *m*-positions in the triazine ring and thus cannot be conjugated through this ring. Any differences in their ultraviolet *y* bands must therefore

be due to variation in the triazine ring absorption caused by the substituent R. All three dyes exhibit anthraquinonoid bands in the 240—260 mμ region, and a band in the 300—320 mμ region for which $\lambda_{max.}$ and hence electron mobility increases with decrease in electronegativity of R, and which is thus due to triazine ring absorption. This progressively enhanced electron mobility affects the electron repellency of the imino-nitrogen atoms and consequently causes an even greater progressive bathochromic shift of the visible *x* band. These dyes do not exhibit a weak absorption band, nor is there any appreciable solvent effect. The relation of the spectra of the *leuco*-dyes to those of the dyes themselves is similar to that of the preceding two groups. Visual examination reveals a strong fluorescence emission, which must affect the measurements considerably.



(IX) : a; R = Cl b; R = Br (X) : a; R = H b; R = Br (XI)

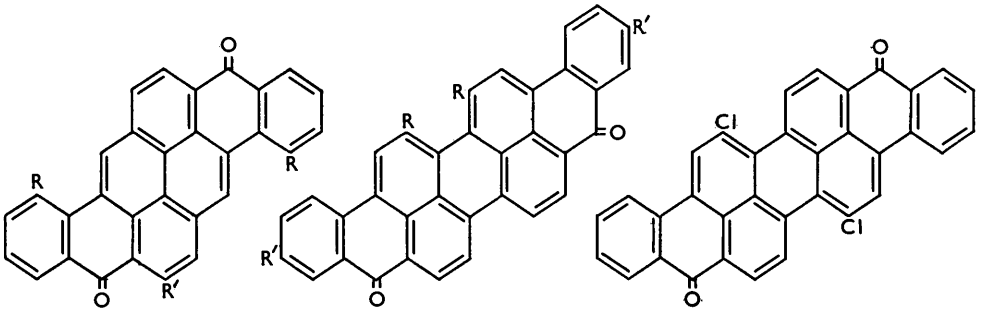
Anthanthrones and Dibenzopyrenequinones.—The spectra of the anthanthrones Cibanone Brilliant Orange GK (IXa) and RK (IXb), and of the dibenzopyrenequinones Cibanone Golden Yellow GK (Xa) and RK (Xb) are all very similar. Surprisingly, the visible *x* band is at longer wavelengths for the first pair than for the second, which have longer lateral molecular extension, two more conjugation electrons, and more dipolar contributory resonance structures. The explanation may lie in the difference in the conjugation of the carbonyl groups. The two carbonyl-bearing rings are fused in anthanthrone, and linked similarly to diphenyl in dibenzopyrenequinone; electron mobility in the *x* direction should thus be greater in the former. For the ultraviolet *y* bands, the absorbing system is probably restricted to one carbonyl group, as in (XI), because of the mutual interference of the electron-attracting properties of the two carbonyl groups. The occurrence of structure (XI) in both anthanthrones and dibenzopyrenequinones explains the similarity of their *y* bands, which also resemble those of anthraquinone.

Only minor spectral changes occur for both pairs on change of the solvent to chlorobenzene, indicating little association of dye with ethanol, but the colour change of the anthranthrones on dilution in ethanol indicates some self-association of solute. Fluorescence is very evident for both pairs, which also exhibit weak absorption bands in the 370—400 mμ region. The *leuco*-solutions again exhibit two main peaks, presumably displaced *x* and *y* bands, the varying relative intensities of which are probably due to differences in the effects of the halogen substituents.

Pyranthrones.—Caledon Gold Orange G (XIIa), Caledon Orange 2RTS = Cibanone Gold Orange 2R (XIIb), and Caledon Brilliant Orange 4RN (XIIc) give broadly similar spectra. The similarity between the central group of six fused rings in (XII) and structure (IX) may explain the similarity of the spectra of the pyranthrones and the anthanthrones, and to a lesser extent those of the dibenzopyrenequinones. The visible *x* band may be

ascribed to absorption along the longer axis of the central groups of six fused rings; the terminal positions of the oxygen atoms along this axis would explain the observed bathochromic shift of the *x* band relative to that of the anthanthrones, while the extreme angularly fused benzene rings should have only minor effects on the *x* band. The ultraviolet *y* bands are generally similar to those of the anthanthrones and dibenzopyrenequinones. The positive detection of weak absorption bands in the 400 mμ region was rendered difficult by the low solubility of the three dyes; however some weak bands were observed at wavelengths much longer than found in any of the preceding dyes. Change of solvent to chlorobenzene caused an unusual bathochromic shift, suggesting a dye-association effect.

The spectra of the *leuco*-dyes exhibit only a single band. The correctness of the above interpretation of the *x* band of the unreduced dyes being assumed, the explanation may be that polar structures contribute significantly to their state, so that the introduction of ionic charges by reduction does not cause such large bathochromic shifts as with the dyes already discussed.



(XII) : a ; R = R′ = H (XIII) : a ; R = R′ = H (XIV)

b ; R = Br, R′ = H b ; R = MeO, R′ = H

c ; R = R′ = Br c ; R = R′ = Cl

Dibenzanthrones.—Caledon Dark Blue 2R (XIII*a*), Caledon Jade Green XN (XIIIb), and Caledon Brilliant Purple 4RN (XIV) all exhibit a strong absorption band near 420—440 mμ. Comparison of the first two dyes shows that substitution by methoxy-groups causes a bathochromic shift throughout the spectrum, which, despite structural isomerism, is broadly similar to that of the third dye. Jade Green XN is dichromatic in hot chlorobenzene but not in cold chlorobenzene or hot or cold ethanol; the *leuco*-solution also exhibits blue-red dichromatism. The dichromatism of the dye is either a thermochroic effect, or more probably a thermally promoted fluorescence of red light after absorption of violet light followed by energy degradation. The visible spectrum of the acid *leuco*-form strongly resembles that of the dye, which is thus spectrally similar to the parent hydrocarbon.

Brilliant Purple 4RN is purple with red fluorescence in saturated solution in chlorobenzene; on dilution, the colour changes through red to yellow, which is the colour in ethanol at all accessible concentrations. The yellow solutions, which absorb strongly in the violet, indicate the presence of a strongly bound dye–solvent complex, which renders detailed interpretation of the spectra difficult.

The unreduced and *leuco*-forms of Cibanone Navy Blue RA (probably XIIIc) have spectra broadly similar to those of Caledon Dark Blue 2R.

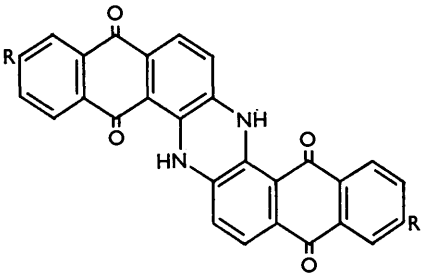
Indanthrones.—The spectral similarity of Caledon Blue RN (= Cibanone Blue RSN; XVa) and Caledon Blue RC (XVb) indicates that chlorination has little effect beyond causing a slight hypsochromic shift in the visible bands of the dye and its *leuco*-derivative. The deep colour of these dyes, despite the interposition of chromophore-insulating NH

groups between the anthraquinone groups, is difficult to explain. Neither hydrogen bonding between nitrogen and oxygen atom, nor a highly polar ground state (suggested by the similar visible spectra of Blue RN and its *leuco*-derivative) can be invoked, because of their inapplicability to the *NN'*-dimethyl derivative of Blue RN, which is similar in spectrum and colour.

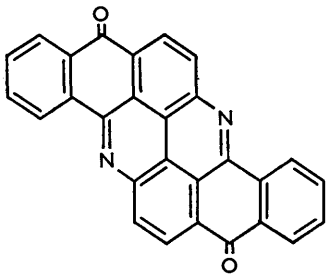
The usual bathochromic shift due to ethanol was observed for these dyes. Their low solubilities rendered detection of weak absorption bands difficult, but there is some indication of such bands in the 670 mμ region.

Flavanthrones.—The spectrum of Caledon Yellow GN (= flavanthrone; XVI) resembles that of Caledon Gold Orange G (= pyranthrone; XII*a*), apart from a bathochromic shift; this is to be expected because of the equivalence of –N= and –CH= despite their different electronegativities. The spectrum of *leuco*-flavanthrone differs from that of *leuco*-pyranthrone, however, perhaps because of the ease of over-reduction of flavanthrone. The usual solvent effect of ethanol was observed for flavanthrone. Low solubility prevented observation of weak absorption bands.

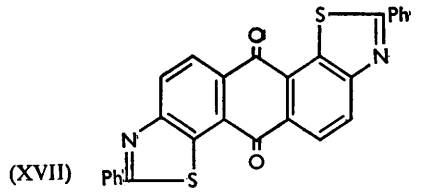
Caledon Yellow 2R is probably a substituted flavanthrone; its spectra generally resemble those of the latter.



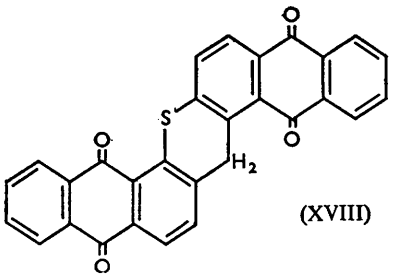
(XV) : a ; R = H b ; R = Cl



(XVI)



(XVII)



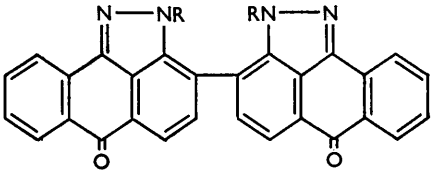
(XVIII)

Miscellaneous Dyes with Fused Heterocyclic Rings.—Caledon Yellow 5G (XVII) is spectrally broadly similar to Cibanone Yellow GK (1 : 5-dibenzamidoanthraquinone); this is to be expected in view of the approximate equivalence of the 1- and the 2-position of anthraquinone, and the structural similarity of the dye (XVII) and the tautomeric imidol form of 2 : 6-dibenzamidoanthraquinone. In Cibanone Orange R (XVIII), the electromeric effect of the insulating sulphur atom, and possible slight hyperconjugation of the methylene-bridge result in a spectrum similar to that of anthraquinone with the α bands shifted slightly bathochromically. In ethanol, this dye becomes greener on dilution; the weak 437 mμ band exhibited only by concentrated solutions is ascribed to a dimer, the formation of which results in self-quenching of the fluorescence emitted by the monomer at lower concentrations.[29] The *leuco*-solution exhibits, unexpectedly, only a single peak in the visible region.

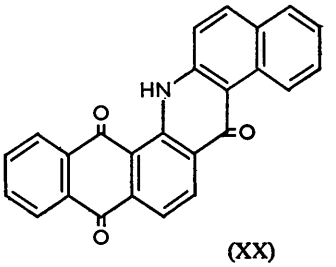
In Cibanone Red 2B (XIX), steric hindrance of the bulky R groups should inhibit coplanarity and therefore mutual conjugation of the two anthraquinone groups. Consequently, the spectra should resemble those of 1-aminoanthraquinone. The ultraviolet

[29] Pringsheim, " Fluorescence and Phosphorescence," Interscience, New York, 1949, p. 390.

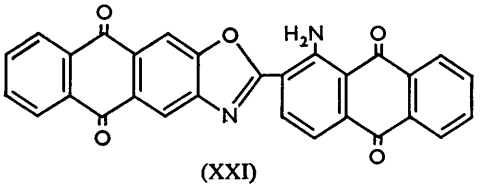
spectrum of the solution and the visible spectrum of dyed cellulose acetate films show this resemblance. The visible spectra of the solutions, however, differ from expectation, indicating strong association of dye with solvent, particularly ethanol; the solutions in ethanol are yellow, and in chlorobenzene orange-yellow. In both solvents, a strong green fluorescence appears increasingly on dilution. No regions of weak absorption were observed. The considerable bathochromic shift accompanying conversion into *leuco*-form suggests that an unusually extensive change of molecular structure occurs.



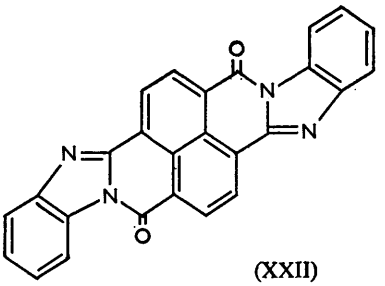
(XIX ; R = sec.-alkyl or alkoxyalkyl)



(XX)



(XXI)



(XXII)

Cibanone Red RK (XX) gives spectra broadly similar to those of 1-benzamidoanthraquinone, illustrating the insulating effect of the carbonyl group in the nitrogen-bearing ring. Solvent effects indicate strong association with ethanol, as with Cibanone Red 2B; the fluorescence behaviour on dilution is also similar to that of the latter dye. Cibanone Red FBB (XXI) again is spectrally similar to the 1-aminoanthraquinone series, indicating unexpected lack of conjugation between the two anthraquinone groups. Absorption peaks for solutions, even of the *leuco*-form, were difficult to locate owing to diffuseness; dyed cellulose acetate films give far more satisfactory spectra.

Indanthren Brilliant Orange GR (XXII), which is not strictly anthraquinonoid, is orange as might be expected from the resemblance of its central ring structure to the pyrene molecule. It gives complicated spectra with ill-defined peaks, which cannot be interpreted satisfactorily in the absence of suitable reference substances. It was found that alkaline reduction produces, according to conditions, either a green or a violet solution, the latter being too labile for spectral examination. The two products may be related either as quinol and semiquinone, or as anthraquinol and oxanthranol analogues.

Relation between Solution Spectra and Fading and Tendering Activity.—The data in Table 2 show that there is no obvious relation between wavelengths of bands in visible spectra and fading or tendering activity. However, several of the dyes exhibit very weak absorption bands, attributed to singlet–triplet transitions. No inactive dye exhibits such bands, although it must be pointed out that the latter may have escaped detection for some dyes exhibiting low solubility or diffuse spectra. The widespread occurrence of these bands indicates that their presence alone is insufficient to account for photoactivity. The varying activities of the acylamino-anthraquinones, despite the fact that they all exhibit weak bands in the same spectral region, emphasise this point.

Table 2 shows that many inactive dyes absorb in the same spectral region as active dyes.

Thus earlier workers [1, 13] have emphasised unduly the importance of the energy of the main singlet–singlet transition, *e.g.* of a band in the 360—400 mμ region. Photoactivity requires another property, which enables absorbed light energy to be utilised for chemical

TABLE 2. *Fading and tendering activity in relation to absorption in the visible and near ultraviolet regions.*

	$\lambda_{max.}$ in ethanol (mμ)	Light fastness [a]	Tendering activity [b]
1-Aminoanthraquinone	*406*, *478*, 497	—	A
1 : 5-Diaminoanthraquinone	*410*, *440*, 492	—	A
1 : 4 : 5-Triaminoanthraquinone	~*410*, *535*, 564, ~*590*	2	—
Algol Yellow WG	408, 430·5	4	A
Caledon Red 5G	*356*, *415*, *477*, *513*, 538, *570*	1	G
Caledon Yellow 3G	371, 407, 425, 465, *496*	1	G
Caledon Red X5BS	*355*, 406, *491*, 538, *570*, *590*	1	—
Caledon Yellow 5GK	*410*, 426, *435*	2	G
Caledon Yellow 4G	403, *427*, *469*, 490	2	E
Indanthren Yellow FFRK	408, 438	1	G
Caledon Olive 1R	*418*, *469*, 505, *568*	1	D
Caledon Gold Orange 3G	*440*, 464, 493, *532*	1	C
Cibanone Yellow 3R	*408*, 421, *440*	1	A
Cibanone Yellow 2GR	427·5, *445*	3	G
Cibanone Red G	*435*, 473, *498*, *520*	2	B
Cibanone Red 4B	*415*, 485, *542*	2	B
Cibanone Brilliant Orange GK	*365*, *468*, 515, 528	1	F
Cibanone Brilliant Orange RK	*375*, 480, 520, 533	1	F
Cibanone Golden Yellow GK	*386*, *415*, 435, 465	2	G
Cibanone Golden Yellow RK	*409*, 415, 435, 464	1	C
Caledon Gold Orange G	418, 432, *482*	3	G
Caledon Orange 2RTS	*405*, *426*, 441, *450*, *475*, 479	2	C
Caledon Brilliant Orange 4RN	*424*, 450, 476, 550	1	C
Caledon Dark Blue 2R	362, 444, 556	1	B
Caledon Jade Green XN	350, *370*, 416, *482*, *538*, ~610, *660*	1	B
Caledon Brilliant Purple 4RN	365, 422, 570	3	B
Caledon Blue RN	371, 442, 482, *554*, 598, 635	1	B
Caledon Blue RC	420, 609, 668	1	B
Caledon Yellow GN	440, *470*	2	A
Caledon Yellow 5G	400	3	H
Cibanone Orange R	422, *437*	3	G
Cibanone Red 2B	*408*, 448	2	B
Cibanone Red RK	*424*, 451·5, *541*	1	C
Cibanone Red FBB	*350*, *418*, 429, ~450	1	F
Indanthren Brilliant Orange GR	*374*, 440, 486, 544, *603*	1	C

[a] Light fastness [7, 8]: 1, v. good; 2, good; 3, moderate; 4, low. [b] Tendering activity [7, 8]: A, none; B, probably none; C, low; D, probably low; E, mild; F, moderate; G, high; H, very high.

reaction, and not degraded to heat. Fluorescence, frequently encountered with these dyes, indicates that the absorbed energy is not degraded to heat, but is retained for *ca.* 10^{-8} sec. as electronic energy not readily convertible into translational energy by collision, and is then re-emitted at a lower frequency after loss of energy by conversion into vibrational energy. Bowen [30] has expressed the need for investigating the relation of fluorescence to photo-activity in dyes, but few spectral as distinct from visual qualitative data on dye fluorescence have been published. The next paper in this series presents some spectral data on the fluorescence of several vat dyes.

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[30] Bowen, "Chemical Aspects of Light," Oxford Univ. Press, 2nd. edn. 1946, p. 164; *J. Soc. Dyers and Col.*, 1949, **65**, 613.