J Forensic Sci, Apr. 1974, Vol. 19, No. 2

T. J. Siek,[1] *Ph.D.*

Identification of Drugs and Other Toxic Compounds from Their Ultraviolet Spectra. Part I: Ultraviolet Absorption Properties of Sixteen Structural Groups

The fully automatic recording spectrophotometer became a basic instrumental necessity in toxicology and crime laboratories a few years after being marketed. About the same time the infrared spectrophotometer became prominent as an analytical instrument, and indeed infrared spectrophotometry became the most specific method of identification available in most laboratories analyzing organic compounds during the sixties. An enormous amount of literature has been devoted to the interpretation of infrared spectra. Since absorption bands in the infrared region are sharper and more numerous than in the ultraviolet (UV) range, little attention has been given to practical approaches to interpretation of UV spectra. The fact that many compounds have similar and nearly identical spectra can be used as an advantage, since fewer standard spectra are needed than there are compounds to be identified. Matching the spectrum of an unknown to that of a known is in many instances simpler than the same process using infrared data.

The data are presented in this manner: in Table 1 some 156 aromatic drugs and toxic compounds are categorized in such a manner that compounds with the same unsaturated, conjugated molecular skeleton or parts of the molecule responsible for UV absorption are in the same group; in Fig. 1 representative scans of at least one member of each of 16 groups are presented; in the **Appendix** the key features of wavelength absorption maxima (λ_{max}), molar absorptivity (ϵ), pH, and solvent effects are summarized for each group; and in Tables 2 and 3 data on a number of more frequently analyzed compounds in each group are presented. Sixteen structural groups are examined in this paper; an additional 38 groups will be dealt with subsequently.

Definition of Terms Used

Pertinent reviews on the principles of ultraviolet spectrophotometry are given by Silverstein and Bassler [*1*] and by Manning [*2*]. Units, symbols, and definitions in spectrometry used in this paper are reviewed below.

Absorbance (*A*)—$A = \log_{10}$ (1/transmittance); also, $A = \epsilon bc$, where ϵ is molar absorptivity; b is length of cell path, cm; and c is concentration, moles per litre.

$E_{1\ cm}^{1\%}$—The absorbance of a 1 percent solution (weight per volume) of a compound in a 1-cm cell. Therefore, $\epsilon = (E_{1\ cm}^{1\%})\ (0.1)$ (molecular weight).

Received for publication 30 April 1973; revised manuscript received 11 Sept. 1973; accepted for publication 3 Oct. 1973.

[1] Virginia Bureau of Forensic Science, Northern Virginia Regional Laboratory, Merrifield, Va.

TABLE 1—*Compounds in the different structural groups.*

A1	Aletamine
	Alverine
	Amphetamine
	Benzphetamine
	Bethanidine
	Cetylpyridium bromide
	Cyclrimine
	Ephedrine
	Hydroxyphenamate
	Mephentermine
	Methamphetamine
	Phendimetrazine
	Phenelzine
	β-Phenethylamine
	Phenformin
	Pheniprazine
	Phenmetrazine
	Phenprobamate
	Phentermine
	Phenylalanine
	2-Phenylethanol
	Phenylpropanolamine
	Procyclidine
	α-Prodeine
	Propoxyphene
	Pseudoephedrine
	Styramate
	Tricyclamol
	Trihexphenidyl
	Trimeperidine
	Toluene
A2	Atropine
	Butethamate
	Carbetapentane
	Caramiphen
	Ethoheptazine
	Ethylmerperidine
	Glycopyrrolate
	Homatropine methylbromide
	Meperidine
	Methscopolamine
	Methylphenidate
	Oxeladin
	Phenylacetic acid
	Scopolamine
A3	Diphenylhydantoin
	Ethotoin
	Glutethimide
	Mephenytoin
	Methetoin
	Methsuximide
	Pemoline
	Phenacemide
	Phensuximide
	Primidone
	Tolazoline
B1	Diphenoxylate
	Dipipanone
	Isomethadone
	Methadone
	Normethadone
	Penicillin G[a]
	Phenadoxone
B2	Adiphenine
	Azacyclonol
	Benactyzine
	Benzhydrol
	Benzilonium bromide
	Benztropine
	Clidinium bromide
	Dextromoramide
	Diphenadol
	Diphenhydramine
	Diphenpyraline
	Doxapram
	Isopropamide
	N-Methyl-3-piperidyl-benzilate
	Pipenzolate bromide
	Piperidolate
	Piperilate
	Pipradrol
	Poldine methylsulfate
C1	Bromdiphenhydramine
	Buclizine
	Chlorcyclizine
	Chlormezanone
	Chlorophenothane (DDT)
	Chlorobenzilate
	Chlorotoluene
	Chlorphenoxamine
	Chlorphentermine
	Cyclizine
	Dichlorobenzene
	Hydroxyzine
	Orphenadrine
	Meclizine
	Tolbutamide[b]
C2	Ketamine
	Pargyline
	Phencyclidine
	Tranylcypromine
D1	Aniline
	Antazoline
	Methaphenilene
D2	Anileridine
D3	*p*-Aminobenzoic acid
	Benoxiate[c]
	Benzocaine
	Benzonatate
	Butacaine
	Butethamine
	Chlorprocaine
	Larocaine
	Metabutoxycaine[c]
	Naepaine
	Procainamide
	Procaine
	Proparacaine[c]
	Propoxycaine[c]
	Tetracaine
E1	Acetophenone
	Benzaldehyde
	Benzophenone
	Diethylpropion
E2	Amitriptyline
	Chlorprothixene
	Doxepin
	Nortriptyline
	Phenindamine
	Pyrobutamine
	Styrene
	Triprolidine
E3	Cyproheptadine
	Protriptyline
	cis-Stilbene
E4	Chloramphenicol
	Nitrazepam
	Nitrobenzene
	p-Nitrotoluene
	Probenecid
	Saccharin
F1	Desipramine
	Imipramine
	Trimipramine
F2	Bufotenine
	Diethyltryptamine
	Dimethyltryptamine
	Ibogaine
	Indole
	Psilocin
	Psilocybin
	Tryptamine
	Serotonin

[a] Max near 320 probably due to *N,N'*-dibenzylethylenediamine chelate compound present in benzathine penicillin G preparations; penicillin *per se* has a weak max near 285 in aqueous solution.

[b] The UV absorption profile of this drug is somewhat atypical for this structural group. The scan in basic solution is similar to compounds in Group A3.

[c] A third ring substituent, an O-alkyl group, does not appreciably alter the UV absorption profile.

Wavelength (λ)—Expressed in nanometre (nm); λ_{max} is a wavelength of maximum absorbance.

Chromophore—A covalently unsaturated group responsible for electronic absorption (for example, C=C, C=O, phenyl).

Auxochrome—A saturated group which, when attached to a chromophore, alters both wavelength and intensity of the absorption maximum (for example, $-CH_3$, $-OH$, $-NH_2$, $-Cl$, $-OR$).

Bathochromic shift—Shift to longer wavelength (red shift).

Hypsochromic shift—Shift to shorter wavelength (blue shift).

Hyperchromic effect—Increased absorption intensity.

Hypochromic effect—Decreased absorption intensity.

K band—$\pi \rightarrow \pi^*$ transitions in aromatic systems in which ϵ is 10,000 or more. In one-ring and biphenylmethyl aromatic systems, two K bands are present, the E_1 and E_2 bands. The E_1 band is generally below 200 nm and the E_2 band above 200 nm.

B band—$\pi \rightarrow \pi^*$ transitions of simple aromatics in which ϵ is generally 100 to 2000 (may be lower or higher in certain cases). The B band is called the "benzenoid band" in much of the literature and has a maximum near 257 nm in aqueous solution, with secondary maxima or shoulders or both which are termed vibrational fine structure.

R band—$n \rightarrow \pi^*$ transitions in which ϵ is less than 100; usually refers to C=O and $-NO_2$ group absorptions.

Homoconjugation—Interaction between seemingly isolated conjugated systems.

Cross conjugation—Two unsaturated bonds conjugated with a third unsaturated bond but not with each other.

Classification of Compounds by Structure and UV Properties

The spectra shown in Fig. 1 were recorded at room temperature on several UV instruments, including the Beckman DK-2A, Acta IV, and DB-G models; the Perkin-Elmer 202; and the Bausch & Lomb 200 UV. Data on compounds in the **Appendix** and Tables 2 and 3 were obtained by the author or abstracted from the references given in the tables. Absorptivity values (ϵ) recorded in Table 2 were calculated from $E_{1\ cm}^{1\%}$ values given in the various references. Publications which tabulate and systematize UV data include Refs *3–15*. Practical discussions on the interpretation of UV data relating to compounds covered here are in Refs *3* and *16–19*. Methods for analysis of specific compounds by UV are reviewed by White [*20*], who covers the literature through 1964.

Group A1 in Table 1 contains the largest number of marketed drugs. Members of Group A1 have the familiar benzenoid band and an E_2 band near 205 nm, which is slightly out of range for many ordinary applications. The minimum between bands for Group A1 is between 225 and 237 nm when scanned in aqueous acid. Spectra shown in the blocks lettered A1, A2, and A3 in Fig. 1 illustrate the spectral differences between groups A1, A2, and A3. Comparison of the spectra of the two A1 compounds in Fig. 1 shows that some minor differences are sometimes apparent within a single group. A1 compounds have no unsaturation in the position beta to the benzene ring (second atom from ring), A2 compounds have a carbonyl group beta to the ring, and A3 compounds have an imide group or nitrogen-containing heterocycle beginning beta to the benzene ring. Representative spectra for each group are shown in Fig. 1. The **Appendix** and Table 2 give pertinent data on Groups A1, A2, and A3, and on the groups discussed below.

Group B1 shows the benzenoid band; in addition a broad band of about the same intensity as the benzenoid band appears near 292 nm in aqueous solution. This band is an R band because it exhibits solvent effects typical of R bands, and compounds in Group

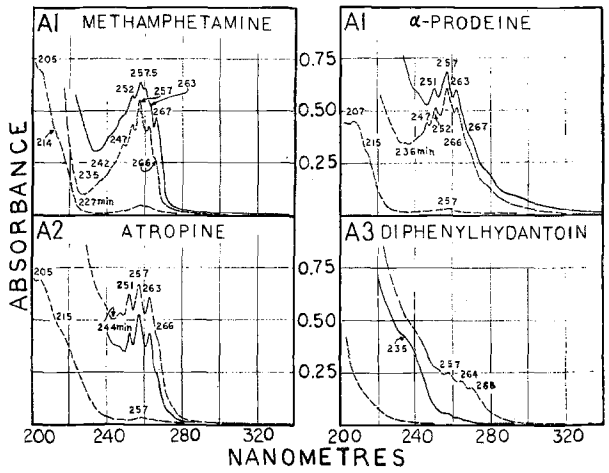


FIG. 1—*Ultraviolet spectra of compounds representative of 16 structural classes. Scans are in aqueous solution unless otherwise noted. The dotted line traces the absorption under acidic conditions and the solid line traces absorption under basic conditions. Concentrations of acid and base are 0.1* N. *Concentrations of individual compounds vary, but can be calculated from molar absorptivity values given in Table 2. Substances absorbing off scale at the lower end of the spectrum at a particular concentration are shown at a second more dilute concentration, so that all bands above 200 nm are represented. Groups A1 through A3 are shown above and Groups B1 through F2 are shown on the opposite page.*

B1 possess the structural segment of phenylacetone (**Appendix**, Group B1) which has E_2, B, and R bands. The position of the E_2 band for Group B1 compounds has not been examined in sufficient detail to include data on λ_{max} in this paper. The B band and the R band are characteristic and diagnostic of Group B1 compounds.

The appearance of Group B2 spectra seems to be quite like that of Group A2. Differences exist in the position of the E_2 band, coming between 210 and 225 in Group B2 and below 212 in Group A2. In addition, some Group B2 compounds have obvious variations of their benzenoid bands. Examples of such are benactyzine, diphenadol, and biphenylmethane.

Both E_2 and B bands are shifted bathochromically in the case of group C1 compounds. An additional ring auxochromic substituent is the causative factor for this shift.[2] The compounds in Group C2 have shifted B bands, but the E_2 band shoulders are below 220 nm.

The D groups are variously substituted aniline derivatives. Compounds of this type in aqueous acid as anilinium salts of the acid used show a decreased absorptivity at a lower wavelength than the unprotonated form in aqueous base or neutral solvent. The pK_a value of an amine group next to an aromatic ring is near 5; therefore, scans at approximately pH 5 and higher will exhibit UV properties of the unprotonated forms. Anileridine is the only compound listed in Group D2; there are no other drugs with this type of ring substitution now marketed in the United States.

The greatly increased absorptivity in nonacidic solution shown by Group D3 may be explained by considering the effect that an electron withdrawing group para to the amino substituent would have, in terms of the interaction of the "lone pair" 2*s* electrons on the nitrogen atom with the ring. In acid solution this electron pair bonds with a proton,

[2] Cyclizine is the only Group C1 compound listed not possessing a second ring substituent. The beta amine nitrogen causes a slight red shift of the benzenoid band.

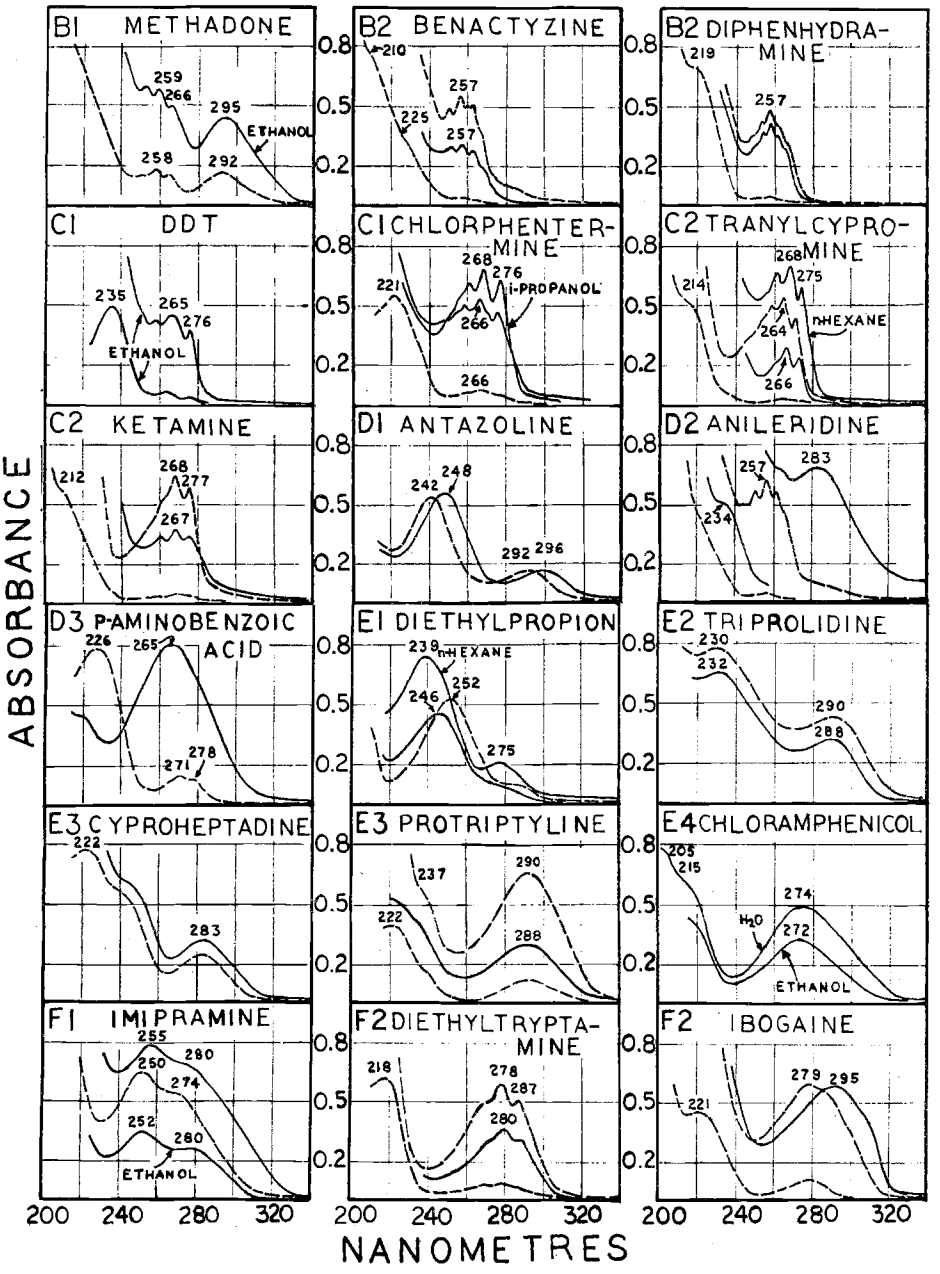

B1 METHADONE
259
266
295
ETHANOL
258
292
B2 BENACTYZINE
210
257
225
257
B2 DIPHENHYDRAMINE
219
257
C1 DDT
235
265
276
ETHANOL
C1 CHLORPHENTERMINE
268
276
i-PROPANOL
221
266
266
C2 TRANYLCYPROMINE
214
268
275
264
nHEXANE
266
C2 KETAMINE
212
268
277
267
D1 ANTAZOLINE
242
248
292
296
D2 ANILERIDINE
257
283
234
D3 P-AMINOBENZOIC ACID
226
265
271
278
E1 DIETHYLPROPION
239
nHEXANE
246
252
275
E2 TRIPROLIDINE
230
232
290
288
E3 CYPROHEPTADINE
222
283
E3 PROTRIPTYLINE
237
290
222
288
E4 CHLORAMPHENICOL
205
215
274
H2O
272
ETHANOL
F1 IMIPRAMINE
255
250
280
274
252
280
ETHANOL
F2 DIETHYLTRYPTAMINE
218
278
287
280
F2 IBOGAINE
279
295
221
0.8
0.5
0.2
ABSORBANCE
200
240
280
320
NANOMETRES

TABLE 2—*UV absorption data on a number of compounds in each of 16 structural groups.*

Compound[a]	Wavelength Max[b] in Aqueous Acid	Aqueous Base	Other[c]	Absorbance Data Wavelength	Molar Absorptivity	Solvent[c]	Ref[d]	Refs to Illustrated spectra
Group A1								
Amphetamine*	257.3 + fine,[e] 205[f]	257 + fine	Min[g]—227	257	192	H_3O^+		4, 5, 6
			hex—257.8 + fine	257	184	H_3O^+[g]	4	
			MeOH—258.2 + fine, 207	257	260	OH^-	4	
				257	202	H_3O^+	3	
				258	190	MeOH	6	
				206	21 000	H_2O	6	
Bethanidine	258 + fine	257 + fine	Min—233	258	230	H_2O	3	3[h]
Benzphetamine	258 + fine	258 + fine	Min—226	258	516	H_3O^+	3	5
Cetypyridinium Chloride	259 + fine, 214	259 + fine, 214	Min—232	259	4 450	H_2O	3	5, 6, 12
Cycrimine	257 + fine	257 + fine	Min—230	257	172	H_3O^+	3	6
				257	206	MeOH	6	
Ephedrine	256.5 + fine	257 + fine	Min—227	257	202	H_3O^+	3	4, 5
Hydroxyphenamate	257 + fine	257 + fine	Min—227	257	182	H_3O^+	3	5
Mephentermine	258 + fine	257 + fine	Min—227	258	160	H_3O^+	4	4, 5
				258	220	OH^-	4	
Methamphetamine*	257 + fine, 205	257 + fine	Min—227	257	210	H_3O^+		4, Fig. 1
				205	14 000	H_3O^+		
Phendimetrazine	257 + fine	256 + fine	Min—235	257	252	H_3O^+	3	5
Phenelzine	257 + fine	257 + fine	Min—226	257	140	H_3O^+	4	4, 5
				258	150	OH^-	4	
β-Phenethylamine*	256.5 + fine	257 + fine	Min—226	257	194	H_3O^+		22
				257	210	OH^-		
Phenmetrazine	256 + fine	256 + fine	Min—228	256	188	H_3O^+	3	5
Phentermine	257 + fine	257 + fine	Min—229	257	276	H_3O^+	3	6
Phenylalanine	257 + fine	257 + fine	Min—233	257	203	H_3O^+	12	12
Phenylpropanolamine	257 + fine	257 + fine	Min—226	257	166	H_3O^+	5	4, 5
Procyclidine	258 + fine	257 + fine	Min—230	258	187	H_3O^+	3	5
α-Prodeine*	257 + fine, 207, 215—inflection	257 + fine	Min—236, EtOH—258 + fine	258	207	H_3O^+	9	Fig. 1
				257	220	H_3O^+		
d-Propoxyphene*	257 + fine	257 + fine	Min—233	257	407	H_3O^+	3	5
Tricyclamol	257 + fine	257 + fine	Min—233	257	189	H_2O	3	7[h]
Trihexphenidyl	257 + fine, 206—shoulder	257 + fine	Min—232 EtOH—251, 256	258	241	H_3O^+	3	6
				257	198	MeOH	6	
Styramate	257 + fine	257 + fine	Min—225	257	197	H_3O^+	3	5

Group A2								
Atropine*	257 + fine, 205	257 + fine	Min—242	257	174	H_3O^+	3	Fig. 1
				257	193	MeOH	6	
				205	8 490	MeOH	6	
Carbetapentane	257 + fine	257 + fine	Min—250	259	116	H_3O^+	3	5, 6
			MeOH—258, 206	258	199	MeOH	6	
Ethoheptazine	257 + fine, 208—shoulder	257 + fine	Min—245	258	209	H_3O^+	3	4, 5
Homatropine methylbromide	257 + fine	257 + fine	Min—248	258	185	EtOH	3	5
Meperidine	257 + fine, 210	257 + fine	Min—247	257	208	EtOH	3	5, 6
			EtOH—258 + fine	257	188	H_3O^+	3	
				257	210	H_2O	9	
Methscopolamine bromide	258 + fine	258 + fine	Min—248	258	190	H_3O^+	5	6
Methylphenidate	257 + fine	258 + fine	Min—243	257	186	H_3O^+	3	4, 5
				257	190	H_3O^+	5	
Phenylacetic acid	257 + fine	258 + fine	Min—240	257	193	H_3O^+	22	22
Scopolamine	257 + fine, 205—shoulder	257 + fine	Min—243	257	273	H_3O^+	5	6
				257	303	OH^-	5	
Group A3								
Diphenylhydantoin*	257 + fine	235	MeOH—258 + fine	235	5 300	OH^-	5	Fig. 1
				257	738	MeOH	3	
Ethotoin	257 + fine	257 + fine	EtOH—257	257	236	EtOH	5	5
Glutethimide	257 + fine	235	Min—250	257	399	EtOH	3	4, 16
			EtOH—257.5 + fine	234	13 500	OH^-	4	
				233	11 000	OH^-	16	
Methetoin	256 + fine	234—shoulder	EtOH—256	256	262	EtOH	5	5
Methsuximide	257 + fine	257 + fine	EtOH—257 + fine	256	366	H_3O^+	3	5
Phenacemide	257 + fine	...	MeOH—257 + fine, 230—shoulder	257	285	MeOH	3	6
				257	305	MeOH	6	
Phensuximide	257 + fine	257 + fine	H_2O—257 + fine	257	284	H_3O^+	3	6
				257	285	MeOH	6	
Primidone	257 + fine	257 + fine	EtOH—258 + fine	258	131	EtOH	3	16, 5
				257	218	H_3O^+	5	
Tolazoline	256 + fine	256 + fine	EtOH—257 + fine	257	240	EtOH	3	5
				256	177	H_3O^+	5	
				256	192	OH^-	5	

(*Continued*)

TABLE 2—Continued

Compound[a]	Wavelength Max[b] in			Absorbance Data				Refs to Illustrated Spectra
	Aqueous Acid	Aqueous Base	Other[c]	Wavelength	Molar Absorptivity	Solvent[c]	Ref[d]	
Group B1								
Diphenoxylate*	257 + fine, 283	···	Min—247	257	1 570	EtOH		6
				283	1 270	EtOH		
Dipipanone	258 + fine, 292	259 + fine, 292	EtOH—259, 294	259	768	OH^-	5	5
				292	489	OH^-	5	
Isomethadone	259 + fine, 292	260 + fine	EtOH—259, 299	259	602	EtOH	5	
				299	618	EtOH	5	
Methadone*	259 + fine, 292	259 + fine, 292	EtOH—260, 295	259	547	H_3O^+	3	Fig. 1, 5
			Min—252	292	519	H_3O^+	3	
Penicillin G	257 + fine, 315	257 + fine, 278, 322	Min—250	257	1 380	MeOH	6	6, 5
Phenadoxone	259 + fine, 292	···	EtOH—259, 296; Min—250	292	570	H_3O^+	3	5
Group B2								
Adiphenine*	258 + fine, 218—inflection	259 + fine	Min—244	258	405	H_3O^+	3	5
Azacyclonol	258 + fine, 220	257 + fine	Min—246	259	454	H_3O^+	3	4, 6
				258	460	H_3O^+	4	
Benactyzine*	257 + fine, 225—inflection, 210—shoulder	257 + fine	Min—248	258	426	H_3O^+	3	6, 5
				257	450	H_3O^+		
Diphenadol*	257, 252, 216	257 + fine	Min—244	259	1 640	H_3O^+	3	
Diphenhydramine*	257 + fine, 219	257 + fine	Min—244	257	460	H_3O^+	3	Fig. 1, 4
				219	9 000	H_3O^+		
Diphenylpyraline	258 + fine, 218—shoulder	258 + fine	Min—244	258	562	H_3O^+	3	4, 5, 6
Doxapram	259 + fine	···	Min—245	259	530	H_3O^+	3	7[h]
Isopropamide iodide	259 + fine, 224—inflection	···	Min—251	259	955	H_3O^+	3	6, 4
Piperidolate	258 + fine, 218—shoulder	258 + fine	Min—243	258	485	H_3O^+	3	6
Pipenzolate bromide	258 + fine, shoulders below 225	···	Min—249	258	482	H_3O^+	3	6
Pipethanate	258 + fine	···	Min—248	258	452	H_3O^+	3	6
Pipradrol	257 + fine, 219	257 + fine	Min—245	258	454	H_3O^+	3	4, 5, 6
				258	440	H_3O^+	4	

Group C1								
Chlorcyclizine	232, 263.5 + fine	229, 261 + fine	EtOH—230, 263 + fine	263	751	H_3O^+	3	4, 5
				230	14 900	EtOH	3	
				232	18 900	H_3O^+	3	
Chlormezanone	227, 265 + fine	259 + fine	EtOH—227, 264 + fine	265	630	H_3O^+	3	4, 5
				266	640	H_3O^+	4	
Chlorobenzene*	211, 265 + fine	265 + fine	HC—210, 267 + fine	210	7 400	HC	17	
			EtOH—210, 265	267	200	HC	17	
Chlorophenothane* (DDT)	236, 266 + fine	...	EtOH—236, 267 + fine	230	12 900	H_3O^+	3	Fig. 1
Chlorphentermine*	221, 265 + fine	266 + fine	*i*-prop—222, 268 + fine	266	202	H_3O^+	5	Fig. 1
				267	221	EtOH	15	
				220	9 700	EtOH	15	
Cyclizine	224, 262 + fine	227, 259 + fine	MeOH—259 + fine	262	666	H_3O^+	3	4, 5
				225	10 480	H_3O^+	3	
Hydroxyzine	230, 263 + fine	230, 260 + fine	...	263	750	H_3O^+	3	4, 5
				232	15 700	H_3O^+	3	
Meclizine*	231, 266 + fine	...	EtOH—230, 266 + fine	230	15 600	H_3O^+	3	4, 5
				266	1 330	H_3O^+	3	
Orphenadrine*	220—inflection, 263 + fine	264 + fine	...	263	646	H_3O^+	3	5
				263	670	H_3O^+	4	
Tolbutamide	228, 262.5 + fine	...	EtOH—227, 262 + fine	228	13 500	EtOH	3	12
				262	704	EtOH	3	
Group C2								
Ketamine*	268 + fine, 212—inflection	267 + fine	Min—239	268	327	H_3O^+		Fig. 1
				267	150	OH^-		
Pargyline	261 + fine	257 + fine	Min—229	261	238	H_3O^+	5	
				257	143	OH^-	5	
Phencyclidine*	262.5 + fine, 220—inflection	263 + fine	EtOH—262 + fine, Min—229	263	299	H_3O^+	3	
Tranylcypromine*	264 + fine, 214—inflection	266 + fine	hex—268, 275; Min—236	264	216	H_3O^+	3	Fig. 1
Group D1								
Antazoline*	242, 290	248, 296	EtOH—242, 290	241	10 870	H_2O	3	4, 5
				292	1 322	H_2O	3	
Methapheniline	240, 292	248, 296	EtOH—243, 293	243	15 130	EtOH	3	4, 5
				240	13 000	H_3O^+	4	
Group D2								
Anileridine*	257 + fine, 222—inflection	234, 284	234, 285 at pH 7	258	444	H_3O^+	3	Fig. 1

(*Continued*)

TABLE 2—Continued

Compound[a]	Wavelength Max[b] in			Absorbance Data				Refs to Illustrated spectra
	Aqueous Acid	Aqueous Base	Other[c]	Wavelength	Molar Absorptivity	Solvent[c]	Ref[d]	
Group D3								
p-Aminobenzoic acid*	225, 271, 278	221, 265	EtOH—228, 289	226	12 300	H_3O^+	18	Fig. 1
				270	970	H_3O^+	18	
				265	14 900	OH^-	18	
Benoxinate	230, 280, 307	225, 307	MeOH—225, 280, 273, 323	323	2 370	MeOH	6	5, 6
				224	20 200	MeOH	6	
Benzocaine*	225, 270, 277	221, 284	EtOH—293, 220; hex—270, 279, 220—shoulder, 214	225	11 600	H_3O^+		4, 5, 6
				270	2 480	H_3O^+		
				284	15 600	OH^-		
				219	8 920	OH^-		
Benzonatate	226, 308	...	EtOH—226, 308	225	6 870	MeOH	6	6
				308	26 800	MeOH	6	
Metabutoxycaine	229, 285	222, 318	MeOH—224, 320	313	2 070	H_2O	5	5
Naepaine	227, 273, 279, 290	294.5, 220.5	MeOH—222.5, 297	273	2 080	H_3O^+	3	6
				279	2 100	H_3O^+	3	
				290	1 530	H_3O^+	3	
Procainamide*	225, 271	275	...	275	16 300	OH^-	3	5
				224	10 930	H_3O^+	3	
Procaine*	228, 272, 279	225, 287	Hex—271, 280, 223—shoulder	279	1 417	H_3O^+	3	4, 5
				290	16 000	H_2O	3	
				228	14 000	H_3O^+	4	
				280	3 000	H_3O^+	4	
Proparacaine	231, 268, 311	231, 265, 311	EtOH—232, 267, 314	231	21 650	H_2O	5	6
				268	7 960	H_2O	5	
				310	4 340	H_2O	5	
Tetracaine*	228, 279, 273, 310	230, 310	...	310	2 540	H_3O^+	5	4
				306	2 900	OH^-	5	
				228	14 500	H_3O^+	4	
Group E1								
Benzaldehyde	246, 280, 289—shoulder	hex—244, 248, 280	EtOH—242, 280, 328	244	15 000	EtOH	1	6
				240	16 000	EtOH	17	
				280	1 660	EtOH	17	
				328	20	EtOH	17	

Benzophenone*	255, 203—shoulder	255	EtOH—252, 330	252	19 300	EtOH		
			hex—247	330	183	EtOH		
				252	20 000	EtOH	1	
				325	180	EtOH	1	
Diethylpropion*	252, 292	246, 292	hex—240, 275, 300	246	9 440	OH^-	3	4, Fig. 1
				253	11 900	H_3O^+	3	
Group E2								
Amitriptyline*	239, 272	238, 274	EtOH—242	240	13 900	H_3O^+	3	
				238	12 600	EtOH	14	
Chlorprothixene	229, 268, 324	...	...	324	2 840	H_3O^+	5	5
				325	2 810	H_3O^+	14	
Doxepin*	255, 292	255, 292	...	255	8 300	H_3O^+		
				292	3 400	H_3O^+		
Nortriptyline*	239, 273	238	MeOH—239	240	12 380	H_3O^+	3	
				239	12 630	MeOH	3	
Phenindamine	220, 258, 280—shoulder	262	MeOH—220, 260, 282	259	8 280	H_3O^+	3	4, 6
				261	6 110	EtOH	14	
Pyrrobutamine	227, 240—shoulder	...	MeOH—225, 240—shoulder	227	7 250	H_3O^+	3	6
Triprolidine*	230, 290	232, 288	MeOH—234, 281	230	7 610	H_3O^+	3	Fig. 1, 6
				234	15 200	MeOH	6	
				281	7 300	MeOH	6	
Group E3								
Cyproheptidene*	224, 241, 283	220, 246, 283	*i*-prop—220, 240, 283	224	47 600	H_3O^+	3	Fig. 1
				285	10 200	H_3O^+	3	
Protriptyline*	223, 238, 290	222, 238, 288	*i*-prop—220, 240, 283	223	28 000	H_3O^+		Fig. 1
				290	13 400	H_3O^+		
Group E4								
Chloramphenicol*	274, 215, 205—shoulders	276	EtOH—271, 215—shoulder	278	9 630	H_2O	3	6, 12
				276	6 455	OH^-	3	
				271	12 920	EtOH		
Nitrazepam	277, 340	...	EtOH—253, 275	278	42 200	H_3O^+	3	
Nitrotoluene*	283, 216	283	EtOH—272	285	10 000	H_2O	13	
				217	6 300	H_2O	13	
Saccharin*	224, 231, 245, 279, 287	234, 265, 285	MeOH—222—shoulder, 275, 285	235	6 430	OH^-	3	6
				268	1 640	OH^-	3	
				275	1 080	MeOH	6	

(*Continued*)

TABLE 2—Continued

Compound[a]	Wavelength Max[b] in: Aqueous Acid	Aqueous Base	Other[c]	Absorbance Data: Wavelength	Molar Absorptivity	Solvent[c]	Ref[d]	Refs to Illustrated Spectra
Group F1								
Desipramine*	250, 274	253, 276	EtOH—252, 276	251	9 690	H_3O^+	3	5
				274	7 840	H_3O^+	3	
Imipramine*	250, 273	255, 276	EtOH—253, 275	250	6 670	H_3O^+	3	Fig. 1
Trimipramine	250, 268	...	...	250	8 830	H_3O^+	3	
				268	7 370	H_3O^+	3	
Group F2								
Bufotenine*	220, 274, 295—shoulder	226, 272, 320	220, 275, 300, 310—shoulder	223	22 400	EtOH	3	6
				277	6 610	EtOH	3	
				277	5 490	H_3O^+	21	
				296	4 600	H_3O^+	21	
Diethyltryptamine* (DET)	219, 272, 278, 287	219, 273, 280, 287	EtOH—226, 276, 282, 290	218	29 000	H_3O^+	23	Fig. 1
				277	7 190	H_3O^+	23	
Dimethyltryptamine (DMT)	218, 272, 278, 287	218, 272, 280, 287	EtOH—276, 282, 292	281	6 390	EtOH	14	6
				282	5 850	MeOH	23	
Ibogaine*	221, 279, 294—shoulder	220, 295	MeOH—225, 290	227	33 000	EtOH	18	Fig. 1
				292	7 260	EtOH	18	
Psilocin*	220, 269, 281, 291	270, 299	EtOH—222, 268, 285, 294	222	38 000	EtOH	21	
				268	5 630	EtOH	21	
				285	4 680	EtOH	21	
				294	4 360	EtOH	21	
Psilocybin	220, 269, 277, 290	269, 290	MeOH—220, 267; EtOH—220, 266	220	32 000	EtOH	21	
				266	6 020	EtOH	21	
Tryptophan	279	292	EtOH—223, 280, 290	223	33 000	EtOH	18	
				280	5 620	EtOH	18	
				290	5 000	EtOH	18	

[a] Compounds are listed by the groups given in Table 1. Starred (*) compounds were UV-analyzed by the author; maxima and minima for other compounds were obtained from references given in the last two columns.

[b] The underlined max is the most intense one where more than one max is given for a compound.

[c] Abbreviations for solvents: H_3O^+ is dilute (0.05 to 0.5 *N*) aqueous mineral acid, OH^- is dilute (0.05 to 0.5 *N*) aqueous sodium hydroxide, EtOH is 95 percent ethanol, MeOH is methanol, hex is *n*-hexane, HC is hydrocarbon such as *iso*octane, and *i*-prop is isopropanol.

[d] Absorbance data given without a reference were determined by the author.

[e] "Fine" denotes a benzenoid band with secondary maxima or shoulders or both in addition to λ_{max}. Refer to Fig. 1 for examples of compounds with benzenoid bands.

[f] This maxima, the "E_2 band," is present in compounds in groups A1, A2, A3, B1, and B2; however, it has been studied only with the few compounds where it is listed in this table.

[g] Minima are given for aqueous acid solution, since aqueous base and other organic solvents show "end absorption" near the wavelength region where minima are given.

[h] Spectra are not illustrated; maxima and minima data are given.

negating interaction with the ring. In Groups D1 and D2, neutralization of the anilinium acid salt results in some increased absorptivity, since the lone pair can now interact with the π electrons of the ring. This occurs to an even greater degree when an electron withdrawing group ortho or para to the amino group is present.

With Group E1 the conjugated ring of benzene is extended by a carbonyl function. Molar absorptivity of the major band is near 10,000. There are three bands in the near-UV range; the R band arising from the carbonyl group is too weak for practical purposes, ϵ being less than 50.

Conjugation is extended by a carbon-carbon double bond in Group E2. Cross conjugation exists in several compounds of this group. The number of conjugated double bonds in Group E3 is eight; ϵ values in the mid-UV range are as much as 47,600 (for example, cyproheptadine in Table 2). Group E4 also contains strongly absorbing compounds due to extended conjugation. Compounds in Group E4 do not have a basic similarity in their absorption profiles, since various chromophores are included.

Compounds of Group F1 are tricyclic dibenzazepines and have indistinguishable UV profiles. Compounds in Group F2 are all indole derivatives and exhibit the same major absorption bands, but show individual differences when unlike auxochromic groups are present on the conjugated indole nucleus. Diethyltryptamine and dimethyltryptamine have no structural differences in the UV absorbing parts of the molecule and thus have the same absorption profile.

Most electron transitions given in the **Appendix** are of the $\pi \rightarrow \pi^*$ type, and a few of the $n \rightarrow \pi^*$ type. Saturated amines show $n \rightarrow \sigma^*$ transitions of moderate intensity near 200 nm, with ϵ about 4000 [*16*]. Thus, part of the absorption below 215 in compounds containing isolated amine groups is due to $n \rightarrow \sigma^*$ transitions, and may well determine the position and shape of E_2 bands in many bases, amides, and imides. Since the position of a minimum is fixed by λ_{max} and ϵ_{max} of the B band and E_2 band, positions of minima are nearly as useful as the positions of E_2 bands themselves, which are often out of range.

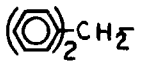
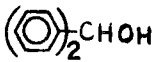
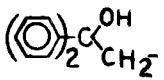
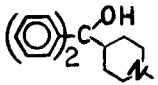
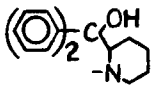
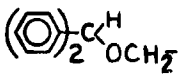
Using UV Profiles and Tables of Data for Identification

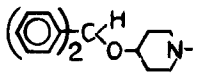
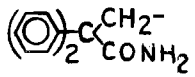
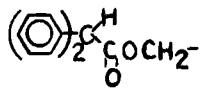
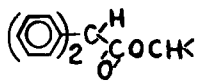
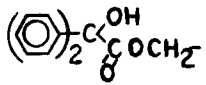
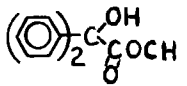
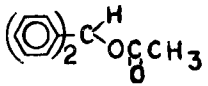
A step-by-step approach to identification from the data in this paper and from other published UV data might be somewhat as follows: (1) obtain evidence that the substance under investigation contains only one UV absorbing compound; (2) record the spectra in aqueous acid, base, and a less polar solvent such as 95 percent ethanol, isopropanol, or hexane; (3) find one or more close matches of the compound in question with spectra in Fig. 1; (4) make a list of possibilities with reference to Tables 1, 2, and 3 and the **Appendix**; and (5) choose analytical methods to differentiate compounds on the possibility list.

Table 2 details UV characteristics of 150 drugs and toxins, covering the more widely used and/or abused compounds of each structural group. Examination of the literature often reveals discrepancies in $E_{1\ cm}^{1\%}$ and ϵ values reported by different authors. The molar absorptivity in a specified solvent for a compound of a particular structural type can be anticipated by noting ϵ values of other compounds of the same structural type. Absorptivities for a single substance reported by different investigators can be expected to vary as much as 20 percent due to differences in instruments used and slit width settings. Obviously erroneous values given in the literature can be excluded from use when ϵ can be approximated from the data in Table 2 and the **Appendix**. Absorptivity values given here are for the compounds themselves and not for salts or hydrates thereof.

It is important to recognize that a methylene unit or other saturated carbon atom will not insulate a chromophore from interaction with an aromatic ring. For example, in Group B1 the ketone group has a much higher ϵ than aliphatic ketones in general, due to

TABLE 3—*Minor variations in UV absorption bands of Group B2 compounds.*

Structure[a]	Compound	Max	Benzenoid Band Secondary Maxima[b]	Min	Lower Band	Solvent	Ref
	Diphenylmethane	261	259, 268, 253, 254, 248 (max); 264 (shoulder)	243	216—inflection	95% EtOH	author
	Benzhydrol	258	252, 263, 248, 267, 243 (max)	244	216—shoulder	95% EtOH	author
	Diphenadol	252	257 (max); 247, 263, 267 (shoulders)	245	216—shoulder	95% EtOH	author
	Azacyclonol	258	252 (max); 263, 268, 247 (shoulders)	245	220—broad shoulder	0.5 *N* HCl	4, 6
	Pipradrol	257	252 (max); 248, 262, 269 (shoulders)	245	219—broad shoulder	0.5 *N* HCl	4, 6
	Diphenhydramine	257.3	252 (max); 263, 268, 247 (shoulders)	243	219—broad shoulder	0.1 *N* HCl	Fig. 1

	Diphenylpyraline	257	251 (max); 263, 268, 247 (shoulders)	244	218—max or broad shoulder	MeOH/HCl	4, 6
	Isopropamide Iodide	259	263, 252 (max); 269 (shoulder)	251	220, 212—shoulders	MeOH/HCl	6
	Adiphenine	258	253, 265, 248 (max); 269 (shoulder)	243	218—inflection	0.1 *N* HCl	author
	Piperidolate	258	253, 265, 248 (max); 269 (shoulder)	245	218—inflection	MeOH/HCl	4
	Benactyzine	257	251, 261, 263 (max); 267 (shoulder)	248	225, 210—inflections	0.5 *N* HCl	Fig. 1
	*N*-Methyl-3-piperidylbenzilate	257	252, 261, 263 (max); 268 (shoulder)	248	···	0.1 *N* HCl	author
	Benzhydrolacetate	256.4	251, 261, 246, 265, 242 (max)	243	216—shoulder	95% EtOH	author

[a] The part of molecular structure which prescribes the UV absorption configuration is shown. Absorption maxima are given for compounds named in Column 2.
[b] Secondary max in decreasing order of intensity.

interaction with the π electrons of the benzene ring. Auxochromic groups greatly influence λ_{max} and fine structure of the benzenoid band. Toluene, amphetamine, *o*-xylene, *m*-xylene, and *p*-xylene differ from each other in appearance of the benzenoid band. Extension of the carbon chain of alkylbenzenes with saturated atoms beyond two carbons results in a common UV profile, which is like that of amphetamine. The minimum for both monoalkylbenzenes and biphenylmethyl derivatives is a function of the type of atom beta to the ring. This becomes clear upon studying spectra of the A, B, and C groups.

The position of the E_2 band, as well as the shape of the benzenoid band in Group B2, varies with the type of substitution alpha and beta to the aromatic rings. Table 3 examines this situation. An actual comparison of spectra of the different structural types in Group B2 will reveal differences in shape or symmetry of the benzenoid bands; some substances show more distinct secondary bands than others.

Generalizations Regarding Spectra-Structure Correlations

Inspection of spectra within the structure groups presented here, along with previously reported observations, permit certain empirical guidelines to be made. These are: (1) if conjugated parts and substituents extending through three atoms from the conjugated parts in two molecules are the same, their UV absorption patterns will be indistinguishable; (2) two saturated carbon atoms extending from a conjugated part of a molecule will effectively shield the conjugated part from interaction with auxochromes and simple chromophores extending from the beta (second in chain) carbon atom; (3) aromatic rings substituted with auxochromic and chromophoric groups which can hydrogen bond will show pronounced spectra changes in going from water to less polar solvents; and (4) protonation with aqueous acid of a nitrogen which is alpha to a conjugated center will be accompanied by decreased absorptivity and a blue shift.

This paper is to be followed by Part II, which will treat other structural groups with respect to UV absorption characteristics. The effect of solvent and pH change on ϵ and λ_{max} will be considered further.

Summary

The ultraviolet absorption spectra of 16 different types of substituted benzene derivatives was examined. Compounds studied include drugs which are currently used and abused and organic substances noted for their toxicity. In general, it was found that compounds with the same conjugated molecular system and adjacent auxochrome and/or chromophore groups had very similar, if not identical, ultraviolet spectra from about 200 to 360 nm. Therefore, compounds with similarities of chemical structure and ultraviolet spectra were placed in designated groups. The ultraviolet properties of approximately 160 compounds were studied in forming the groups. Some of the individual groups include monoalkylbenzenes, biphenylmethyl derivatives, disubstituted benzenes, substituted biphenylmethyl derivatives, variously substituted aniline derivatives, and benzene derivatives in which conjugation is extended beyond the ring. Absorption maxima and minima, molar absorptivities, and effects of solvent change and pH change were studied for each of the 16 groups.

APPENDIX

Classification of Ultraviolet Absorbing Compounds According to Molecular Structure and Absorption Properties

Group A1—Monoalkylbenzene derivatives with saturated bonds extending at least through two atoms from position of ring attachment.

1. Maxima and Minima.[3]
   a. 257.5 ± 1.5 and at or near 252, 263, 247, 242, 236, and 267—the benzenoid band.[4]
      (1) Secondary bands decrease in intensity with distance from λ_{max}.
      (2) pH change has only slight or no apparent effect on λ_{max} at 257; some changes in secondary max may be noted.
      (3) λ_{max} shifts with solvent change less than 2 nm.
      (4) $E_{1\ cm}^{1\%}$ range is 4–28.
   b. 203–209 max with inflection(s) or shoulder(s).
      (1) No substantial fine structure.
      (2) Band is approximately 30 times stronger than benzenoid.
   c. Min between benzenoid and lower band is 225–237; λ_{min} is 227 ± 1 for most A1 compounds.
2. Type of transitions.
   a. 257 is $\pi \rightarrow \pi^*$ B band; ϵ range is 160–400 with average approximately 215 per benzene ring; ϵ is lower when benzene ring is a small part of the molecule.
   b. 205 is $\pi \rightarrow \pi^*$ E_2 band; ϵ is 20 to 80 times benzenoid band.
3. Example—toluene.[5]

λ_{max}	ϵ	Solvent	Ref
262.5	245	0.1 *N* HCl	author
261	248	Methanol	14
206.5	7 900	Methanol	18
261	260	Methanol	18
262	260	Hydrocarbon	17
208	7 900	Hydrocarbon	17

Group A2—Monoalkylbenzene derivatives with saturated α-carbon (α to ring) and β-carbonyl group.

1. Maxima and minima—same as A1 except:
   a. Min between B band and E_2 band is 241–252.
   b. E_2 band is 206–210 and may be only a shoulder (leading to E_1 band below 200).
   c. $E_{1\ cm}^{1\%}$ range is 4–17.
2. Type of transitions—same as A1.

Group A3—Monoalkylbenzene derivatives with saturated α carbon and β-carbonyl group which is part of an imide or cyclic imide, or with another type of nitrogen-containing ring in the beta position.

1. Maxima and minima.
   a. 257.5 ± 1.5 in H_3O^+ or alcohol; $E_{1\ cm}^{1\%}$ range is 4–30.
   b. 235 ± 5 in OH^- for "acidic" imides; $E_{1\ cm}^{1\%}$ range is 200–900.
   c. Absorption increases steadily with decreasing wavelength below the 257 max; very shallow min below 257.
2. Type of transitions.
   a. 257 is $\pi \rightarrow \pi^*$ B band; ϵ is same as A1.
   b. 235 (in OH^-) is $\pi \rightarrow \pi^*$; ϵ is about 10,000.

[3] Wavelengths are given in nanometres with the stronger max underlined. Minima are given for aqueous acid or water solutions. Maxima are given for aqueous solution unless stated otherwise.

[4] Secondary max or fine structure are characteristic of "benzenoid" absorption band. Exact positions and absorbance intensities of these maxima vary with different compounds.

[5] Only Group A1 substance with benzenoid max above 260 nm.

Group B1—Biphenylmethyl derivatives with broad max near 290 in addition to benzenoid band.

1. Maxima and minima.
   a. 259 ± 1 with fine structure (benzenoid).
      (1) pH and solvent changes cause slight or no apparent λ shifts.
      (2) $E_{1\ cm}^{1\%}$ is approximately 18.
   b. 280–295 broad max.
      (1) Shift +2 to 4 in going from H_2O to EtOH.
      (2) $E_{1\ cm}^{1\%}$ is approximately 17 (nearly the same as benzenoid).
   c. Min below benzenoid is 240–252; E_2 band is a shoulder or series of shoulders and inflections below 232.
2. Type of transitions.
   a. 259 is $\pi \rightarrow \pi^*$ B band; ϵ range is 250–550.
   b. 290 is $n \rightarrow \pi^*$ R band; ϵ is ½ to 1 times 259 max (this band is much more intense than the usual R band, since ϵ for acetone is approximately 14).
3. Example—phenylacetone.

Band	λ_{max}	ϵ	Ref
E_2	210	1 200	17
B	257 (in H_2O)	253	author
R	280 (in H_2O)	130	author

Group B2—Biphenylmethyl derivatives with benzenoid band and stronger absorption near 220.

1. Maxima and minima.
   a. 258 ± 2 with fine structure which may have shape unlike Group A1 compounds.
      (1) Moderate λ shifts with solvent and pH changes.
      (2) $E_{1\ cm}^{1\%}$ is approximately 18.
   b. 210–226 single broad band or inflection or one or more shoulders.
      (1) $E_{1\ cm}^{1\%}$ range is 300–500.
      (2) Type of band (true max or shoulder) depends on how α carbon atom is substituted (see Table 3).
3. Type of transitions.
   a. 258 is $\pi \rightarrow \pi^*$ B band; ϵ range is 400–700.
   b. 220 is $\pi \rightarrow \pi^*$ E_2 band; ϵ is about 10,000.

Group C1—Disubstituted benzenes and some biphenylmethyl derivatives, shifted benzenoid band plus broad E_2 band above 220.

1. Maxima and minima.
   a. 261–271 with fine structure; slight shifts of max with solvent and pH changes; $E_{1\ cm}^{1\%}$ range is 25–40.
   b. 220–238 broad max is approximately 20 times more intense than upper band; slight shifts of max with solvent change; $E_{1\ cm}^{1\%}$ range is 320–600.
   c. Min between B and E_2 bands is approximately 251.
2. Type of transitions.
   a. 265 is $\pi \rightarrow \pi^*$ B band; ϵ range is 600–1300; ϵ is less than 400 for compound with one aromatic ring.
   b. 230 is $\pi \rightarrow \pi^*$ E_2 band; ϵ range is 7000–16,000.
3. Examples.

Compound	λ_{max}	ϵ	Solvent	ϵ Ratio, lower/upper	Ref
o-xylene	210	8 300	MeOH/H_2O (50/50)	27.7	13
	262.5	300			
m-xylene	212	7 200	MeOH/H_2O (50/50)	24.0	13
	264.5	300			
p-xylene	212	8 000	hexane	17.4	17
	268.5	460	hexane		

Group C2—Monosubstituted benzene derivatives with α carbon as part of non-aromatic ring; shifted benzenoid with inflection or shoulder below 225.

1. Maxima.
   a. 264 ± 3 plus fine in H_3O^+; $E_{1\,cm}^{1\%}$ range is 12–24; pH and solvent effects on max from 1–4 nm.
   b. 216 ± 4 inflection or shoulder, but no distinct max.
2. Type of transitions.
   a. 263 is $\pi \rightarrow \pi^*$ shifted B band; ϵ range is 210–330 in H_3O^+.
   b. 218 is $\pi \rightarrow \pi^*$ E_2 band (not a max).

Group D1—Aniline derivatives with *N*-substituent and additional unsaturated ring.

1. Maxima.
   a. Strong broad max near 240 in H_3O^+; red shift of 6–9 nm and 5–10 percent increase in ϵ going from H_3O^+ to OH^-.
   b. Weak band near 290 in H_3O^+; red shift of 4–8 nm and approximately 12 percent increase in ϵ going from H_3O^+ to OH^-.
2. Type of transitions.
   a. 240 is $\pi \rightarrow \pi^*$ E_2 band; $E_{1\,cm}^{1\%}$ is about 570 in H_3O^+.
   b. 290 is $\pi \rightarrow \pi^*$ B band; $E_{1\,cm}^{1\%}$ is about 76 in H_3O^+.
3. Example—aniline.

λ_{max}	ϵ	Solvent	Ref
203	7 500	H_3O^+	17
255	160	H_3O^+	17
230	8 600	OH^-	18
280	1 430	OH^-	18
235	···	EtOH	18
286	···	EtOH	18

Group D2—Aniline derivative with ring alkyl substituent.

1. Maxima.
   a. 257 with fine in H_3O^+ (typical benzenoid).
   b. Major band near 234, minor band near 254 in OH^- or neutral solution.
   c. Inflection near 222 in H_3O^+ (partial E_2 band).
2. Type of transitions.
   a. 257 (in H_3O^+) is $\pi \rightarrow \pi^*$ B band; $E_{1\,cm}^{1\%}$ is about 13.
   b. 234 is $\pi \rightarrow \pi^*$ E_2 band; $E_{1\,cm}^{1\%}$ is about 500.
   c. 284 is $\pi \rightarrow \pi^*$ B band; $E_{1\,cm}^{1\%}$ is about 75.

Group D3—Aminobenzoate esters with and without *N*-alkyl substituent.

1. Maxima.
   a. 229 ± 4 major band in H_3O^+; 2–6 nm blue shift in less polar solvents.
   b. 275 ± 5 minor band with upper shoulder ±5 nm from max in H_3O^+.
   c. Strong major band near 286, minor near 223 in OH^- or neutral solution; these bands show moderately large changes in less polar solvents.
   d. *N*-alkyl substituted derivatives have max above 300 in most solvents including aqueous acid and base; primary amine esters with an *O*-alkyl substituent also have max above 300.
2. Type of transitions.
   a. 229 is $\pi \rightarrow \pi^*$ E_2 band; $E_{1\,cm}^{1\%}$ is about 450.
   b. 275 is $\pi \rightarrow \pi^*$ B band; $E_{1\,cm}^{1\%}$ is about 50–110.
   c. 286 is $\pi \rightarrow \pi^*$ B band; $E_{1\,cm}^{1\%}$ is about 900–1400.
   d. 300 is $\pi \rightarrow \pi^*$ B band; $E_{1\,cm}^{1\%}$ is about 1000.

Group E1—Phenylalkylketones and other phenylcarbonyl compounds.

1. Maxima.
   a. Three bands between 235–330 nm with intensity inversely proportional to λ_{max}.
   b. Pronounced blue shift in less polar solvents for lower two bands and red shift for upper band (upper band very weak).

2. Type of transitions.
   a. Lower is $\pi \rightarrow \pi^*$ E_2 band; ϵ is about 13,000.
   b. Middle is $\pi \rightarrow \pi^*$ B band; ϵ is about 1100.
   c. Upper is $\pi \rightarrow \pi^*$ R band; ϵ is about 50.
3. Example—acetophenone.

λ_{max}	ϵ	Solvent	Ref
238	13 000	hexane	17
276	800	hexane	17
320	40	hexane	17
240	...	EtOH	1
278	...	EtOH	1
319	...	EtOH	1

Group E2—Benzene with conjugation extended by ethylene unit (that is, four conjugated carbon-carbon double bonds).

1. Maxima.
   a. 230–250 very strong major band with slight λ_{max} changes with pH and solvent changes.
   b. Secondary band near 280 (weak shoulder only).
2. Type of transitions.
   a. Lower is $\pi \rightarrow \pi^*$ E_2 band; $E_{1\ cm}^{1\%}$ is 250–500.
   b. Upper is $\pi \rightarrow \pi^*$ B band; $E_{1\ cm}^{1\%}$ is about 50.
3. Example—styrene.

λ_{max}	ϵ	Solvent	Ref
244	12 000	EtOH	1
282	450	EtOH	1
248	...	hexane	17
282	...	hexane	17

Group E3—Stilbene-styrene nucleus with additional substituents (7 or more conjugated double bonds).

1. Maxima.
   a. Major band 220–232 nm with moderate pH and solvent effects; $E_{1\ cm}^{1\%}$ 1200.
   b. Second strong band (usually shoulder) near 240 nm.
   c. Band of moderate intensity near 290 nm.
2. Type of transitions.
   a. Lower is $\pi \rightarrow \pi^*$ K band; ϵ is about 25,000.
   b. Middle is $\pi \rightarrow \pi^*$ K band; ϵ is about 20,000.
   c. Upper is $\pi \rightarrow \pi^*$ K band; ϵ is about 10,000.
3. Example—*cis*-stilbene.

λ_{max}	ϵ	Solvent	Ref
222	25 000	EtOH	1
263	12 300	EtOH	1

Group E4—Benzene substituent with unsaturated group other than carbonyl and ethylene—nitro, sulfonyl, azo, and nitroso.

1. Maxima.
   a. Major band of strong intensity 240–290.
      (1) λ_{max} shifts with pH change.
      (2) Blue shift and more fine structure in less polar solvents; moderately large (3–10 nm) shift changing from water to 95 percent ethanol.

b. Two minor bands above major band; second minor band very weak (ϵ is <300) and λ_{max} is above 300; these bands are not apparent in aqueous solution.
c. 210–225 shoulder or max is about half the intensity of the major band.

2. Type of transitions.
   a. Major is $\pi \rightarrow \pi^*$ K band (most likely E_2 band).
   b. Minor below 300 is $\pi \rightarrow \pi^*$ B band.
   c. Minor above 300 is $n \rightarrow \pi$ R band.
3. Example—nitrobenzene.

λ_{max}	ϵ	Solvent	Ref
252	10 000	hexane	1
280	1 000	hexane	1
330	140	hexane	1
267	7 800	H_3O^+	19
212	...	H_2O	author
267	7 350	H_2O	author
260	5 890	95% EtOH	author

Group F1—Dibenzazepins.

1. Maxima.
   a. Major band near 250 with shoulder near 270.
   b. Moderate (4–8 nm) red shift changing from H_3O^+ to OH^-.
   c. Free base (unprotonated amine) in other solvents shows red shift.
   d. Slightly decreased absorption in H_3O^+ (protonated ring N).
2. Type of transition—250 is $\pi \rightarrow \pi^*$ B band; $E_{1\ cm}^{1\%}$ is about 300; ϵ is about 9000.

Group F2—Indoles.

1. Maxima.
   a. Strong band 216–226.
      (1) Slightly decreased absorption in H_3O^+ due to protonation of ring N.
      (2) Slight red shift changing from H_3O^+ to OH^-.
   b. Weaker band near 280 with some fine structures; increased fine structure in less polar solvents accompanied by moderate λ_{max} shifts.
2. Type of transitions.
   a. Lower is $\pi \rightarrow \pi^*$ E_2 band; $E_{1\ cm}^{1\%}$ is about 1500.
   b. Upper is $\pi \rightarrow \pi^*$ B band; $E_{1\ cm}^{1\%}$ range is 260–480.
3. Example—indole.

λ_{max}	ϵ	Solvent	Ref
220	26 000	cyclohexane	18
280	5 620	cyclohexane	18
216	31 600	MeOH	13
271	5 000	MeOH	13

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Commonwealth of Virginia
Bureau of Forensic Science
Northern Virginia Regional Laboratory
2714 Dorr Ave.
Merrifield, Va. 22116