the reaction flask contained 1200 ml. of carbon disulfide and 55 g. of sublimed aluminum chloride. The drip rate from the funnel was adjusted to one-fifteenth that of the reflux rate and the total time of addition was 78 hours. The reaction mixture was stirred vigorously throughout this period. After removal of carbon disulfide and treatment of the residue with ice, the product, 13.5 g., having the physical constants shown in Table II was isolated by steam distillation, extraction, and vacuum distillation. *Anal.* Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.71; H, 7.84.

The ketone formed an oxime, m.p. 92.5°, and a semicarbazone, m.p. 220°. Upon oxidation with permanganate a mixture of phthalic and phthalonic acids was formed.

There was no advantage in the extreme dilution technique as applied to the preparation of benzosuberone which is formed in excellent yield by Plattner's high dilution technique. An attempt to prepare benzocyclononanone by the cyclization of 7-phenylheptanoyl chloride using the extreme dilution technique resulted in the formation of a polymeric product and no volatile ketone was found.

The values for the oscillator strength were derived from ϵ–ν plots by planimetric integration of curves which, in the regions of overlapping, were drawn to zero extinction in a somewhat arbitrary way. The resulting uncertainty is negligible for the strong C bands, but the estimates for the B bands in some cases depend appreciably upon the manner of extrapolating to zero extinction.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUÍMICA, FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS, UNIVERSIDADE DE SÃO PAULO]

Ultraviolet Absorption Spectra of Fully Aromatic Esters and Thiolesters[1]

BY G. CILENTO

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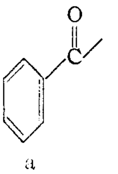
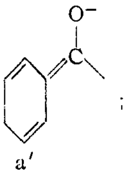
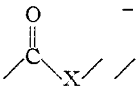
In aromatic esters or thiolesters, three main electronic transitions may be expected, which in several cases might give rise to two systems of cross-conjugation. Although there are some cross-conjugation effects, the electronic transitions are largely independent of one another. A certain band appearing in the spectra of certain thiolesters is attributed to an activated state in which the sulfur atom expands its valence shell to a decet.

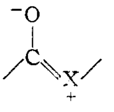
The present paper reports the ultraviolet absorption spectra (above 220 mμ) of 20 phenyl benzoates or phenyl thiolbenzoates substituted in the two para-positions by methoxyl, nitro or chlorine, as listed in Table I.

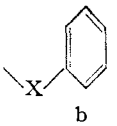
Three main electronic transitions may be anticipated in such molecules: (1) that associated with the aroyl absorption of ring A corresponding to structures a and a'; (2) interaction of ring B with the oxygen or the sulfur atom of the ester grouping (structures b and b'); (3) excitation of the ester group proper, symbolized by c and c'. When R_1 and R_2 are suitable substituents two systems of cross-conjugation may arise, but it appears that the three transitions take place independently although some cross-conjugation effects are present in the spectra.

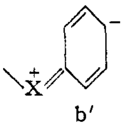

a


a' ;


c


c' ;


b


b'

For an interpretation of the position of the bands observed the following considerations seemed important. The ground state of the transition a,a' might be slightly higher than that found in ordinary aroyl groups because the aroyl resonance a ↔ a' is opposed by the ester resonance c ↔ c', although this effect is to some extent compensated by the resonance b ↔ b' which opposes the ester group resonance. Regarding the excited state a' the same considerations are applicable but are more important, because a' is established at the expense of the strong ester resonance c ↔ c'; thus one would expect a' to be farther from its ground state than, *e.g.*, the excited state of benzaldehyde is from its ground state, and, as above, any weakening of c ↔ c' by effects of ring would reapproximate a' to the ground state a. Perhaps such stabilization of the excited state explains the fact that the benzoyl band of phenyl thiolbenzoate lies at a longer wave length than that of cyclohexyl thiolbenzoate, λ_{max} 239 and 235 mμ, respectively.[2]

Furthermore, Table I shows that nitration of ring B (compounds V and VI) causes bathochromic displacement of the benzoyl absorption. When the A-ring contains methoxyl (Compounds III and IV) the benzoyl maxima are again shifted bathochromically, but on subsequent introduction of NO_2-groups into the B-ring the two aromatic bands overlap although the maximum of the resultant band lies at longer wave length than do any of the bands in the parent compounds III and V; IV and VI,[3]

Thiolesters exhibit aroyl absorption at longer wave length than their oxygen analogs. This is probably due to the stronger tendency of sulfur, as compared to oxygen, to interact with the B-ring; thus the thiolester resonance c ↔ c' would suffer a greater reduction with accompanying stabilization of the excited state a'. Accordingly nitration in the ring B causes a more pronounced red shift of the benzoyl absorption in the case of the thiolester (from 239 to 248 mμ) than in the case of the oxygen ester (from 232 to 235 mμ). It is apparent, however, that there must also be other factors, for phenyl benzoate absorbs at 230 mμ (in C_6H_{12})

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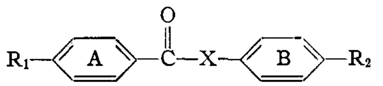
[1] From a paper presented at the 4th meeting of the Sociedade Brasileira para o progresso da Ciência, Porto Alegre, November, 1952.

[2] H. P. Koch, *J. Chem. Soc.*, 387 (1949).

[3] The comparison is not strictly valid in the set of thiolesters IV, VI and VIII, because these were not studied in the same solvent.

TABLE I

RING BANDS OF AROMATIC ESTERS AND THIOLESTERS



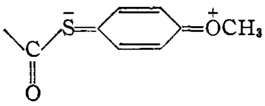
Compounds	Substituents R₁	X	R₂	M.p., °C.	λ_A,[a,b] mμ	$\epsilon_A \times 10^{-3}$	λ_B, mμ	ϵ_B, $\times 10^{-3}$	λ_{A+B}, mμ	$\epsilon_{A+B} \times 10^{-3}$
I	H	O	H	69–70	232	16.3	...	..	...	..
II	H	S	H	55–57	239	17.1	...	..	...	..
II	H	S	H	55–57	239	20.5	...	..	...	..
III	CH_3O	O	H	73.5–75	261	22.2	...	..	...	..
IV	CH_3O	S	H	93–95	286	20.5	...	..	...	..
V	H	O	NO_2	145–146	235	14.1	270	14.3	...	..
VI	H	S	NO_2	126–127	248	16.3	285	13.7	...	..
VI	H	S	NO_2	126–127	248	18.1	285	14.8	...	..
VII	CH_3O	O	NO_2	167–168	...	..	...	..	276	27.4
VIII	CH_3O	S	NO_2	154.4–156	...	..	...	..	292	24.8
IX	H	O	CH_3O	87.5–88.5	228	19.4	...	..	...	..
X	H	S	CH_3O	97.5–99.5	...	..	...	..	242	28.3
XI	CH_3O	O	CH_3O	124–125.5	261	23.5	...	..	...	..
XII	CH_3O	S	CH_3O	134.5–136.5	282	20.8	240	15.3	...	..
XIII	NO_2	O	CH_3O	115–117	258	15.5	...	..	...	..
XIV	NO_2	S	CH_3O	123–125	...	..	...	..	250	19.6
XV	NO_2	O	H	129–130	259	15.4	...	..	...	..
XVI	NO_2	S	H	160–162	260	15.3	...	..	...	..
XVII	NO_2	O	NO_2	160–162	...	..	...	..	266	20.6
XVIII	NO_2	S	NO_2	151.5–153.5	259	22.3	280	17.0	...	..
XIX	Cl	O	Cl	96.5–98	245	23.6	...	..	...	..
XX	Cl	S	Cl	138.5–139.5	249	22.0	...	..	...	..

[a] Subscript A refers to A-ring bands; subscript B refers to the B-ring bands; subscript A + B refers to the bands resulting from the overlapping of A-ring and B-ring bands. [b] All spectra were determined in alcohol except those of VIII and XVIII, which were determined in cyclohexane and hexane, respectively. The spectra of II and VI were determined in both alcohol (first set) and cyclohexane (second set).

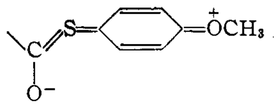
which is a lower value than that for cyclohexyl thiolbenzoate (235 mμ in C_6H_{12}).

Owing to a strong resonance effect in the ester, or thiolester, group, conjugation of the non-bonding *p*-electrons of the heteroatom (X) and the π-electrons of the B-ring is rather weak. Thus the B-ring of *p*-nitrophenyl benzoate (V) causes absorption at 270 mμ, very close to the position of maximal absorption of nitrobenzene itself. Moreover, thiolesters in which R_2 = H exhibits no phenylmercapto band in the spectral range covered, and when $R_2 = NO_2$ the maximum lies at 285 mμ, much lower than the maximum at 338 mμ exhibited by alkyl[4] or aryl *p*-nitrophenyl sulfides.[2,5]

A marked spectral change, however, occurs when methoxyl is introduced into the B-ring of the thiolesters, which causes no pronounced change in the case of the ordinary esters (*cf.* Fig. 1–3); a new band appears at 240 mμ, clearly resolvable in the case of the *p,p*-dimethoxy compound XII.[6] The weakly auxochromic chlorine atom in *p*-chlorophenyl *p*-chlorothiolbenzoate (XX) failed to bring the arylmercapto band into the spectral range studied. The new band is attributed to a transition in which the sulfur atom expands its valence shell to a decet (formulation d) and may be considered a strong indication for the occurrence of this expansion. Even if the negative charge were finally associated with the carbonyl oxygen atom (formulation e), which does not appear likely, a 3d-orbital of the sulfur atom would still be involved. The large literature on the expansion of the sulfur valence shell includes compounds related to those described here, *e.g.*, alkyl aryl sulfides[4]; our thiolesters, however, appear to be the first instance in which sulfur acts equally well as a donor and acceptor; the absorption maxima of both anisole and of nitrobenzene are shifted to a comparable extent in the corresponding aroylmercapto derivatives.



d



e

The –CO–X– band in ordinary esters appears to be non-detectable in our spectra. Either it is very weak and is being overlapped, or, more likely, it is not to be found in the near ultraviolet. Thiolesters, however, show strong absorption agreeing in position and intensity with a band in the spectrum of cyclohexyl thiolbenzoate, attributable to excitation of the –CO–S– system. In many cases, though, this band is more or less masked; in phenyl thiolbenzoate it is resolved ($\lambda_{max}^{ethanol}$ 267 mμ, ε 8,300; $\lambda_{max}^{C_6H_{12}}$ 270 mμ, ε 7,300), but in the spectra of *p*-anisyl thiolbenzoate (X) and of *p*-chlorophenyl *p*-chlorothiolbenzoate (XX) only shoulders are observed (X, about 267 mμ, ε 8,300; XX, 267 mμ, ε 13,700).

It is interesting to note that in aliphatic thiolesters this band lies at about 230 mμ,[7] in cyclo-

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[4] E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 2889 (1949).

[5] (a) H. H. Szmant and J. J. McIntosh, *ibid.*, **73**, 4356 (1951); (b) A. Mahgini and R. Passerini, *J. Chem. Soc.*, 1168 (1952).

[6] For a preliminary report of the observation see G. Cilento, *Experientia*, **8**, 421 (1952).

[7] B. Sjöberg, *Z. physik. Chem.*, **52**, 209 (1942), as cited by H. P. Koch.[8]

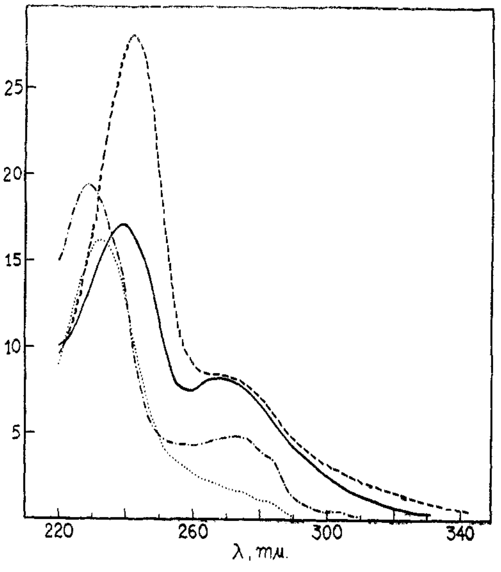

Fig. 1.—Absorption spectra in C_2H_5OH of: C_6H_5-CO-O-C_6H_5, ...; C_6H_5-CO-S-C_6H_5, ———; C_6H_5-CO-O-C_6H_5-OCH_3, -·-·-·-; C_6H_5-CO-S-C_6H_5-OCH_3,----------. The small depression in the main maximum of *p*-anisyl thiolbenzoate reported previously[6] has now been found to be spurious.

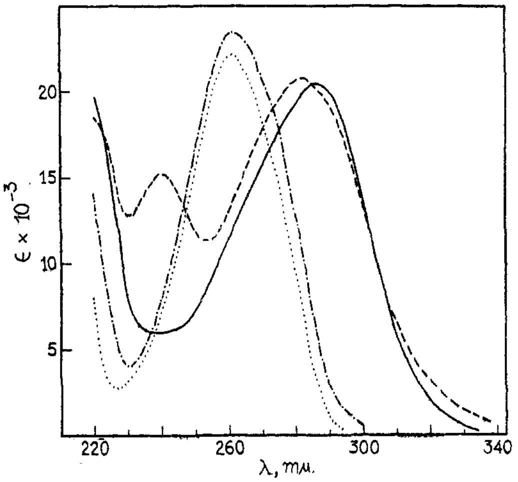

Fig. 2.—Absorption spectra in C_2H_5OH of: CH_3O-C_6H_5-CO-O-C_6H_5, ...; CH_3O-C_6H_5-CO-S-C_6H_5, ———; CH_3O-C_6H_5-CO-O-C_6H_5-OCH_3, -·-·-·-·-; CH_3O-C_6H_5-CO-S-C_6H_5-OCH_3,-----------.

hexyl thiolbenzoate it lies at 268 mμ owing to a ground state effect of the phenyl substitution,[2] and we see now that the second aromatic substitution is without further effect on the position of the thiolester band.

Finally it should be remarked that *p*-anisyl *p*-nitrothiolbenzoate (XIV) is unique among the compounds described in being colored, *i.e.*, yellow, even in solution, with appreciable absorption in the visible.[8]

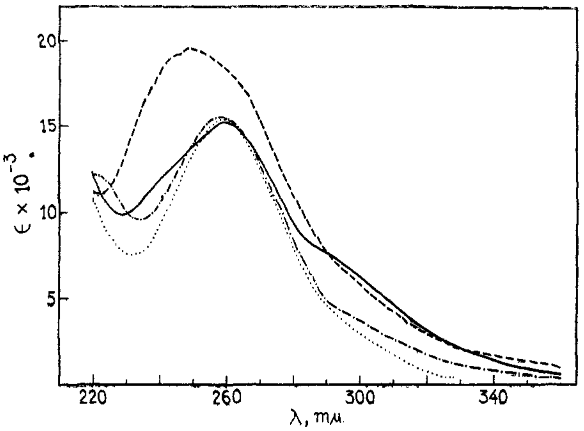

Fig. 3.—Absorption spectra in C_2H_5OH of: O_2N-C_6H_5-CO-O-C_6H_5, ...; O_2N-C_6H_5-CO-S-C_6H_5, ———; O_2N-C_6H_5-CO-O-C_6H_5-OCH_3, -·-·-·-; O_2N-C_6H_5-CO-S-C_6H_5-OCH_3, ----------.

Experimental

The acids, acid chlorides, phenols and mercaptans were prepared by conventional methods or purchased from commercial sources. Esters and thiolesters were obtained by condensation of the phenol or thiophenol with the aroyl chloride. In general pyridine was employed in these condensations. Some of the esters were prepared by addition of thionyl chloride in slight excess to a solution of the acid and the phenol in pyridine. In all cases the mixture was decomposed with water, the product was collected and washed with alkali, acid and water, followed by recrystallization from ethanol and/or benzene. The compounds were dried in an Abderhalden pistol. The melting points were determined on a Kofler apparatus and are included in Table I. The compounds listed below are new and were analyzed.[9]

Cpd.	Formula	Calcd.	Found	Calcd.	Found
VIII	$C_{14}H_{11}O_4SN$	C, 58.12	57.92	H, 3.83	3.63
IX	$C_{14}H_{12}O_3$	C, 73.66	73.49	H, 5.29	5.37
XIII	$C_{14}H_{11}O_5N$			N, 5.13	5.32
XIV	$C_{14}H_{11}O_4SN$	S, 11.08	11.04		
XVIII	$C_{13}H_8O_5SN_2$	C, 51.32	51.19	H, 2.96	2.87

Solvents for spectrophotometry were specially purified. The spectrophotometric data are summarized in Table I, Absorption measurements were carried out with a Beckman DU quartz spectrophotometer. Readings were, in general, taken at 2 mμ intervals, and a constant band width of 10 Å. was employed. Some of the reported extinction values of solutions in non-polar solvents are not very accurate.

Acknowledgment.—The writer is indebted to Dr. P. Manginelli of the Fundacão A. e V. Matarazzo for making available the Beckman spectrophotometer, and he also wishes to express his appreciation to Prof. H. Hauptmann for his helpful criticism. Grateful acknowledgment is also made of the help of Dr. Hans Heyman in the preparation of the manuscript in the format required by THIS JOURNAL.

SAO PAULO, BRAZIL

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(8) G. Cilento, *J. Phys. Colloid Chem.*, **55**, **716** (1951), reported the formation of yellow molecular complexes from nitrated, fully aromatic esters and thiolesters. We have tested the compounds here described for complex formation by dissolving pairs containing at least one nitro compound in acetone, and then evaporating the solvent. Compounds XIV, XIX and XX were not included. In four out of the more than one hundred instances formation of a yellow evaporation residue indicated complex formation: XIII and XVII; XIII and VII; XIII and XVIII; XVIII and XII. A preliminary experiment gave yellow crystals on cooling of a hot solution of XIII and XVIII; possibly other complexes may also be obtainable in this manner.

(9) Microanalyses for C, H and N by Dr. K. Ritter, Analytisches Laboratorium, Basel, Switzerland.