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ELECTRONIC ABSORPTION SPECTRA OF SELENOPHENE ANALOGS OF CHALCONES

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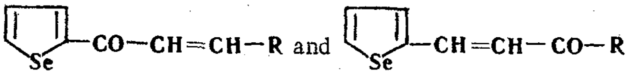
The electronic absorption spectra of 21 1-(selenienyl-2)-3-arylpropen-1-ones and -3-ones are measured in hexane and ethanol solution. It is found that the 2-selenienyl group in such compounds is more bathochromic and electron-donating than 2-furyl and 2-thienyl. The effects of electron-donating and-accepting substituents on λ_{max} of a longwave band are considered. It is shown that Hammett's σ can be connected with shift in absorption frequency when electron-donating substituents are introduced into the aromatic ring of 1-(selenienyl-2)-3-phenylpropen-1-one. The synthesis of three new selenophene analogs of chalcones is described.

Previous publications have dealt with the results of research on the electronic absorption spectra of furan [1], thiophene [2, 3], pyrrole [4] and quinoline [5] analogs of chalcones. It was of interest to study the electronic spectra of selenophene chalcones. Only one paper [6] has been published on the electronic spectra of α, β-unsaturated ketones containing the selenophene group, and it describes the spectra of 2-selenienylideneacetone and its bromo derivative.

We have measured the UV and visible absorption spectra, in hexane and ethanol, of 1-(selenienyl-2)-3-arylpropenones of the type



R—phenyl (I, II), 4-tolyl (III, IV), 4-methoxyphenyl (V, VI), 2,4-dimethoxyphenyl (VII, VIII), 2,4,6-trimethoxyphenyl (IX, X), 4-hydroxyphenyl (XI), 4-aminophenyl (XII), 4-dimethylaminophenyl (XIII, XIV), 4-fluorophenyl (XV), 4-chlorophenyl (XVI, XVII), 4-nitrophenyl (XVIII, XIX), and 4-xenyl (XX, XXI).

Table 1 gives basic spectral properties of the compounds investigated, and the most characteristic absorption plots are shown in Figs. 1 and 2.

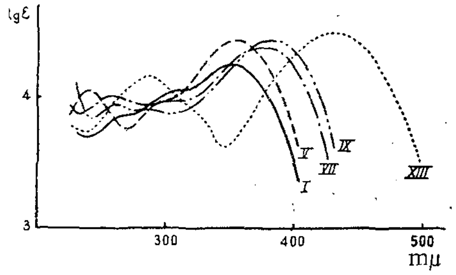


Fig. 1. Absorption curves of ketones I, V, VII, IX, and XIII in ethanol.

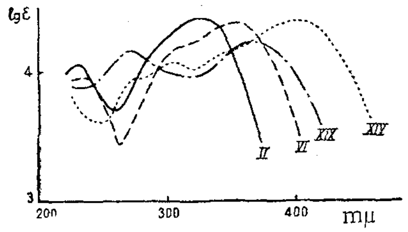


Fig. 2. Absorption curves of ketones II, VI, XIV, and XIX in ethanol.

The spectra of all the ketones show two or three well-defined absorption bands. The most intense band (ε = = 15 000—36 000 is also the longwave one, in the 315-430 mμ region, and due to $\pi - \pi^*$ electron transitions in the longest conjugated chain. It is characteristic that on passing from hexane solutions to ethanol ones, this band is shifted by 10-40 mμ towards the red region because of hydrogen bond formation. The second and third absorption bands are considerably less intense, and by origin, are connected with the appearance of semi-independent separate chromophores [7]. An interesting peculiarity of the spectra of 1-(selenienyl-2)-3-arylpropen-3-ones is the presence, in most cases of a well defined band in the 300-320 mμ region, not shown by their isologs, the furan, thiophene, and pyrrole chalcones.

As compared with the analogous aromatic compounds, the selenophene ketones absorb in a longer wavelength region of the spectrum. Here replacement of phenyl by 2-selenienyl remote from the carbonyl group in the chalcone (λ_{max} in EtOH 312 mμ) gives rise to a bathochromic effect amounting to 40 mμ, but the like replacement adjacent to the carbonyl gives one of 13 mμ (see II and I, respectively). It is known that in α, β-unsaturated ketones electron-

Table 1

Spectrum Properties of 1-(Selenienyl-2)-3-arylpropenones

Aryl	Propen-1-ones								Propen-3-ones						
	Compound Number	Hexane				Ethanol			Compound Number	Hexane			Ethanol		
		λ_{max}, mμ/ε_{max}								λ_{max}, mμ/ε_{max}					
Phenyl	I	315 27500			229 10500	325 26300		230 12900	II	339 18600	299 12000	265 8700	352 18400	312 10400	269 7300
4-Tolyl	III	323 28800	~285 inflection		233 11200	338 28000	~285 inflection	236 11000	IV	339 20000	298 14400	~230 inflection	351 20000	307 14000	
4-Methoxyphenyl	V	338 27500	287 9100		235 11700	355 27500	~295 inflection	240 11100	VI	336 23400	305 18600	234 12300	354 24000	~312 inflection	235 9200
2, 4-Dimethoxyphenyl	VII	350 20400			252 10200	376 25000	302 9400	259 10300	VIII	338 21900	~300 inflection	235 8500	354 22700	~310 inflection	~240 inflection
2, 4, 6-Trimethoxyphenyl	IX	353 20000			257 11200	382 28100	284 8100	261 8900	X	327 15100	~300 inflection	~235 inflection	339 18600	~305 inflection	
4-Hydroxyphenyl	XI	333*	~290 inflection		233	362 25100	293 7900	242 7900							
4-Aminophenyl	XII	362*	272		242	412 26300	284 10900	234 4300							
4-Dimethylaminophenyl	XIII	393 32000	~320 inflection	280 13800	~255 inflection	432 31300	~325 inflection	288 14700	XIV	370 29500	307 11700	267 10500	402 28200	308 11700	274 9300
4-Fluorophenyl	XV	316 28200			227 14500	327 25500		231 10000							
4-Chlorophenyl	XVI	319 24000			230 11000	330 29000		232 10500	XVII	343 22400	300 14100	275 12300	355 20200	303 12500	
4-Nitrophenyl	XVIII	316*			~250 inflection	327 29400		~245 inflection	XIX	355*	313	268	368 17300		272 14900
4-Xenyl	XX	334 36200	266 11500		238 11200	348 35600	268 9400	242 9500	XXI	342 24500	307 21900	237 11500	356 25700	319 20800	231 12600

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* Due to the low solubilities of these compounds in hexane, measurements were qualitative.

donating groups give rise to a more considerable red shift when remote from the carbonyl group [1, 2, 8]. So 2-selenienyl exhibits an electron-donating effect. It is of interest that, under similar circumstances, 2-furyl and 2-thienyl give rise to a somewhat less bathochromic shift (28 and 30 mμ, respectively). This supports a conclusion which we previously drew from study of IR spectra and dipole moments [9], that in the static state the positive conjugation effect decreases in the order 2-selenienyl > 2-thienyl > 2-furyl and this is probably explained to a considerable extent by the large polarizability of the selenophene ring as compared with the thiophene and furan ones.

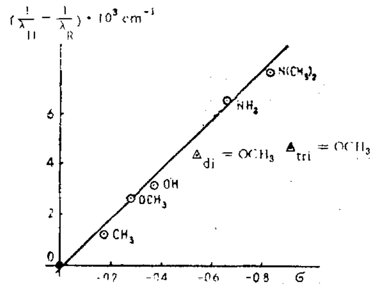


Fig. 3. Relationship between λ_{max} and σ constants for 1-(selenienyl-2)-arylpropen-1-ones.

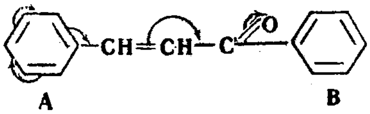
Shift of a carbonyl group from a less to a more nucleophilic ring should result in a red shift of the longwave absorption band [1, 2]. Considering λ_{max} of ketones I-VIII from this point of view, it is seen that 2-selenienyl is, in respect to its electronic character, identical, for example, with 4-methoxyphenyl.

The results in Table 1 show that introduction of an electron-donating substituent into the aromatic ring, with the latter remote from the carbonyl group (see I, III, V, VII, IX, XI, XIII), gives rise to a bathochromic shift which is greater, the more marked its nucleophilic effect. The value of this shift in cm^{-1} correlates satisfactorily with the σ constants of McDaniel and Brown [10], Campbell and Gilow's equation

$$\left(\frac{1}{\lambda_H}-\frac{1}{\lambda_R}\right)\frac{h\cdot c}{2.3\,KT}=\rho\sigma.$$

holding. Table 2 and Fig. 3 give relevant data. The ρ constant for 1-(selenienyl-2)-3-arylpropen-1-ones is 20.4 ± 0.1 differing comparatively little from ρ values calculated for 4-substituted chalcones (22.6 ± 0.1) [4].

Such correlation shows that the longwave absorption band is basically conditioned by electronic transitions, and that the more the electron density is displaced from ring A towards the carbonyl group, the more readily transition to the excited state occurs:



Donor substituents in ring B show a small effect on λ_{max} of the longwave band (see II, IV, VI, VII). Only such a powerful auxochrome as the dimethylamino group (XIV) gives a 31-50 mμ bathochromic shift. Pile-up of methoxyl groups in the aromatic ring (see V-X), i.e., their further introduction at the ortho position, in the case of the propen-1-ones, leads to an always decreasing bathochromic effect. Thus if introduction of the first methoxyl (see I and V) displaces λ_{max} by 23-30 mμ, the second one does so by only 12-21 mμ, and the third by only 3-6 mμ in all. With propen-3-ones, in the case of X, a hypsochromic effect is even observed, accompanied by a decrease in absorption intensity. All this indicates that methoxyl group introduced in the ortho position, give rise to steric hindrance, which is particularly marked with propen-3-ones. A similar steric effect is found in the furan and thiophene series [1, 2].

With regard to electron-accepting substituents (halogens, nitro groups), they, on the contrary, evoke a bathochromic shift if they are in a ring, next to the carbonyl group (see XV - XIX), while with propen-1-ones, they do not exhibit a large effect on the absorption.

Ketone XX absorbs 19-23 mμ further in the longwave region than does I, and here this is due to lengthening of the conjugated chain due to the second ring. On the other hand λ_{max} for XVI differs but little from λ_{max} for II, thus confirming the previously expressed [1, 2] opinion that to a cor

Table 2

Data for Correlation of Electronic Spectra of 1-(selenienyl-2)-arylpropen-1-ones.

Aryl	σ	$\frac{1}{\lambda_H}-\frac{1}{\lambda_R}$, cm⁻¹
Phenyl	0	0
4-Tolyl	−0.17	1180
4-Methoxyphenyl	−0.268	2600
2, 4, -Dimethoxyphenyl	−0.536*	4170
2, 4, 6-Trimethoxyphenyl	−0.804*	4590
4-Hydroxy phenyl	−0.370	3150
4-Aminophenyl	−0.660	6300
4-Dimethylaminophenyl	−0.83	7628

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* σ for o-methoxyphenyl is arbitrarily assumed equal to σ-para-, and because of steric hindrance (see Fig. 3), ρ is not assumed in the calculation.

siderable extent the carbonyl group behaves as an isolator of conjugation.

Experimental

With the exceptions of XI, XII, and XV, the synthesis of the selenophene analogs of chalcones has been described in [12].

1-(Selenienyl-2)-3-(4-hydroxyphenyl)propen-1-one(XI). Equimolecular (0.01 mole) amounts 2-acetylselenophene and 4-hydroxybenzaldehyde were dissolved in 10 ml MeOH, previously saturated at 0° C with HCl gas, and left at room temperature. After 5 hr the resultant dark solution was poured into 50 ml water, and left overnight. The dark precipitate was filtered off and recrystallized from 70% aqueous MeOH, using active charcoal. Yield 50%. Yellow needles, mp 171° C. Found: Se 28.33, 28.29%. Calculated for $C_{13}H_{10}O_2Se$: Se 28.49%.

2,4-Dinitrophenylhydrazone, mp 248° C, λ_{max} in $CHCl_3$ 418 mμ. Found: Se 16.92, 16.95%. Calculated for $C_{19}H_{16}N_4O_5Se$: Se 17.27%.

1-(Selenienyl-2)-3-(4-aminophenyl)propen-1-one(XII). A mixture of 0.5 g 1-(selenienyl-2)-3-(4-nitrophenyl) propen-1-one, 2.5 g $SnCl_2$, and 2.5 ml concentrated HCl was heated on a water-bath for 30 min. After cooling the precipitate was filtered off, washed with concentrated HCl, neutralized with ammonia, and recrystallized from MeOH. Yield 80%. Yellow parallelopipeds mp 161° C. Found: Se 28.44, 28.56%. Calculated for $C_{13}H_{11}NOSe$: Se 28.59%.

1-(Selenienyl-2)-3-(4-fluorophenyl) propen-1-one(XV). Prepared by crotonoid condensation of 2-acetylselenophene with 4-fluorobenzaldehyde in the presence of 10% NaOH solution, as described in [12]. Yield 56%. Pale yellow parallelopipeds, mp 123° C (ex MeOH). Found: Se 28.19, 28.33%. Calculated for $C_{13}H_9FOSe$: Se 28.28%.

2,4-Dinitrophenylhydrazone: mp 230° C, λ_{max} in $CHCl_3$ 410 mμ. Found: Se 17.28, 17.24. Calculated foi $C_{19}H_{13}FN_4O_4Se$: Se 17.19%.

The IR and visible region absorption spectra of the compounds under investigation were measured with a SF-4 quartz spectrometer, using a concentration of substance equal to $2-4 \times 10^{-5}$ mole/ℓ. The solvents used (hexane, EtOH), were purified as described in [13].

REFERENCES

1. V. F. Lavrushin, S. V. Tsukerman, and A. I. Artemenko, ZhOKh, 32, 2551, 1962; 33, 878, 3258, 1963; 34, 487, 1964.
2. V. F. Lavrushin, S. V. Tsukerman, and V. M. Nikitchenko, ZhOKh, 32, 2677, 3971, 1962; 33, 1255, 2563, 1963.
3. S. V. Tsukerman, I. K. Gintse, and V. F. Lavrushin, ZhOKh, 34, 2317, 1964.
4. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], 387, 1966.
5. S. V. Tsukerman and Ch'ang Quoc Shuon, KhGS [Chemistry of Heterocyclic Compounds] 366, 537, 1965; Zh. Prikl. spektr., 6, 554, 1966.
6. L. Chierici and G. Papalardo, Gass. Chim. Ital., 90, 69, 1960.
7. D. N. Shigorin, N. Sh. Shcheglova, and N. S. Dokunikhin, DAN, 137, 1416, 1961.
8. H. Szmant and A. J. Basso, J. Am. Chem. Soc., 74, 4397, 1952.
9. S. V. Tsukerman, V. D. Orlov, V. M. Nikitchenko, Yu. S. Rozum, V. P. Lavrushin, and Yu. K. Yur'ev, Teoret. i eksper. khim. [Theoretical and Experimental Chemistry] 2, 399, 1966.
10. D. H. McDaniel and H. C. Brown, J. Org. Chem., 23, 420, 1958.
11. R. Campbell and H. M. Gilow, J. Am. Chem. Soc., 82, 5426, 1960.
12. S. V. Tsukerman, V. D. Orlov, V. F. Lavrushin, and Yu. K. Yur'ev, ZhOrKh, 1, 650, 1965.
13. A. Weissberger, Organic Solvents [Russian translation], IL, Moscow, 275, 308, 1958.

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