DIPOLE MOMENTS OF SELENOPHENE ANALOGS OF THE CHALCONES

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The dipole moments of 24 selenophene analogs of the chalcones have been measured and have been compared with the data calculated by a vectorial additive scheme and also with their chemical structures. Considerations are expressed on the conformational state of the molecules of the compounds investigated. The existence of a correlation between the dipole moments the intramolecular distances, and the Hammett's σ-parameters has been shown. The applicability of Higashi's equation to the calculation of μ for α, β-unsaturated ketones is pointed out.

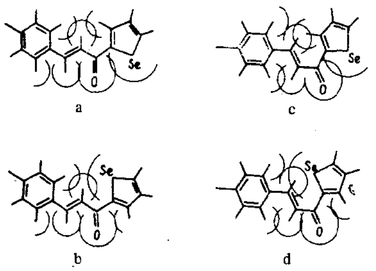
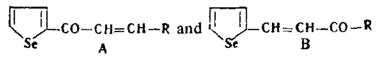


Fig. 1. 1-(2-Selenienyl)-3-phenylpropen-1-one (I): a) syn-s-cis form; b) anti-s-cis form; c) syn-s-trans form; d) anti-s-trans form.

The results of investigations of the dipole moments of chalcones [1] and their furan [2], thiophene [3], pyrrole [4], and quinoline [5] analogs have been reported previously. Continuing our study of α,β-unsaturated ketones, we decided to determine the electric moments of selenophene analogs of the chalcones of types A and B (table):



There is information in the literature on values of μ only for selenophene [6-8] and some of its simplest derivatives [8]. For the majority of the compounds that we investigated, the dipole moments for the possible coplanar conformations were calculated by the vectorial additive scheme. In these calculations, the moment of the selenophene ring was taken as 0.42 D in the direction along the axis of symmetry toward the heteroatom. The angles and interatomic distances in the selenophene ring were taken from the paper of Mario et al. [9]. The remaining figures required for the calculations were those used previously [1-5]. To evaluate the possible steric effects qualitatively, schemes of the possible planar conformations were constructed using the van der Waals and covalent radii for compounds I and II (Fig. 1).

In a study of the IR spectra of the selenophene analogs of the chalcones [10] it was shown that, with respect to the arrangement of the substituents on the aliphatic double bond, they are trans isomers, and the carbonyl group is in the s-cis position with respect to the neighboring vinylene group. As can be seen from Fig. 1, steric hindrance for the s-cis form is less than for the s-trans form, which is the reason for the predominant existance of the cis conformer. Two coplanar conformations are still possible for the s-cis isomers of ketones I-XIX, differing from one another by the fact that the selenium and oxygen atoms are arranged on the same side (syn form) or on different sides (anti form) of the bond connecting the selenienyl group to the carbonyl group.

From a comparison of the values of μ found for I and II with the calculated values for the syn-s-cis and anti-s-cis forms it follows that they are equally probable and in solution approximately equal amounts of the two conformers exist. The fact that the experimentally determined value of μ for the two conformers must be due to the effect of the interaction of the electron-donating heterocyclic radical [11] with the electron-accepting carbonyl group. The introduction of substituents into the aromatic nucleus of the selenophene chalcones, just as for their thiophene analogs [3], apparently has no effect on the conformational state of the molecules, and for the isomeric ketones the changes in the dipole moments due to this lie on a straight line (Fig. 2).

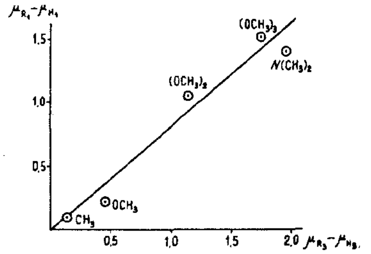


Fig. 2. Relationship between the dipole moments of the isomeric selenophene chalcones: $\mu_{R_1} - \mu_{H_1}$ for the propen-1-ones; $\mu_{R_3} - \mu_{H_3}$ for the propen-3-ones.

For the chalcone analogs XX-XXIV containing two heterocyclic radicals, the existence of four coplanar conformations is possible: syn-syn, syn-anti, anti-syn, Dipole Moments of Selenophene Analogs of the Chalcones

Compound	Type of chalcone	R	α	β	P_∞, cm³	MR_D, cm³	μ, D			
							found	calculated for the		according to Higashi [14]
								syn	anti	
								s-cis forms		
I	A	C_6H_5	17,43	1,17	309.44	65.46	3.45	3.08	2.43	3,46
II	B	C_6H_5	13.80	1,02	260,68	65.46	3,08	3.08	2.43	3.08
III	A	4-CH_3-C_6H_4	18.72	1.17	333.17	70.08	3.58	3.31	2,65	3.59
IV	B	4-CH_3-C_6H_4	15,01	1,28	275,32	70.08	3.17	3.31	2,65	3,21
V	A	4-CH_3O-C_6H_4	22,16	1,37	385,50	71.73	3.90	3.98	3,20	3,91
VI	B	4-CH_3O-C_6H_4	16,10	1,34	294,96	71.73	3,30	3.98	3.20	3,33
VII	A	2,4-$(CH_3O)_2$-C_6H_3	30,33	1,46	510,58	77,99	4.60	—	—	4.57
VIII	B	2,4-$(CH_3O)_2$-C_6H_3	24,59	1,42	427.47	77.99	4,13	—	—	4,12
IX	A	2,4,6-$(CH_3O)_3$-C_6H_2	38,67	1.54	640,89	84.25	5,21	—	—	5.16
X	B	2,4,6-$(CH_3O)_3$-C_6H_2	30,22	1,57	515.84	84.25	4.59	—	—	4,56
XI	A	4-$(CH_3)_2N$-C_6H_4	41.84	1.32	678,13	78.64	5.41	4,20	3.41	5,37
XII	B	4-$(CH_3)_2N$-C_6H_4	28,97	1.30	489,68	78.64	4.48	4,20	3,41	4.46
XIII	A	4-F-C_6H_4	12.72	1,29	242.73	65.27	2,94	2.42	2.40	2,96
XIV	A	4-Cl-C_6H_4	13,81	1.46	259.13	70,33	3,04	2,50	2,26	3,08
XV	B	4-Cl-C_6H_4	16,60	1.40	301,95	70,33	3,36	2,50	2,26	3.38
XVI*	A	4-NO_2-C_6H_4	29,11	1,24	478,13	71,08	4.45	3,28	3.66	—
XVII	B	4-NO_2-C_6H_4	35,28	1,60	573,89	71,08	4,95	3,28	3.66	4,93
XVIII	A	4-C_6H_5-C_6H_4	17,16	1,58	318,92	89,57	3.35	3,08	2,43	3.44
XIX	B	4-C_6H_5-C_6H_4	15.75	1,61	297,29	89,57	3.18	3,08	2.43	3,27
XX	A	2-C_4H_3O	17,16	1.23	300,22	57,58	3.44	a) 3.78 c) 2,71	b)3.09** d) 1,93	3.44
XXI	B	2-C_4H_3O	15,25	1,24	271.86	57,58	3,23	a) 3,78 c) 2,71	b) 3.09 d) 1,93	3,43
XXII	A	2-C_4H_3S	17,09	1.37	300.40	63,51	3,40	a) 3,61 c) 2,74	b) 2,92 d) 1,98	3,43
XXIII	B	2-C_4H_3S	17,92	1.32	314.12	63,51	3,50	a) 3,61 c) 2,74	b) 2,92 d) 1.98	3,50
XXIV	A	2-C_4H_3Se	16,46	1.96	289,15	67,12	3,29	a) 3,49 c) 2,80	b) 2,80 d) 2,06	3.38

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* In dioxane.

For compounds **XX-XXIV calculations were made for the forms: a) syn-syn; b) anti-syn; c) syn-anti; and d) anti-anti.

and anti-anti. However, it is impossible by comparing the experimental values of μ with those calculated (table) to give preference to any of the possible conformers.

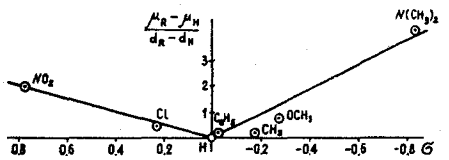

Fig. 3. Relationship between the dipole moments of the 3-aryl-1-(2-selenienyl)-propen-3-ones and the σ-constants of the substituents.

If in chalcone (μ 3.00 D) or in its derivatives [1] a phenyl group adjacent to the carbonyl group is replaced by a 2-selenienyl group (forming a propen-1-one) this leads to an increase in μ by approximately 0.3-0.5 D. The analogous substitution remote from the carbonyl group (propen-3-ones) has very little effect on μ. Probably, in the static state the effect of the interaction of the selenienyl and carbonyl groups is greater when they are adjacent to one another and are not separated by a vinylene group. This fact is confirmed by the IR spectra [10] since the characteristic frequency of the vibrations of the carbonyl group in the propen-1-ones is always lower than in the propen-3-ones. In addition to this, the fact that most frequently the values of μ for the propen-1-ones are considerably greater than for their isomers, in particular for compounds XI and XII containing a dimethylamino group, can probably be explained in part by the assumption that in these cases the syn-s-cis conformations predominate somewhat in solutions.

As a rule the dipole moments of the selenophene analogs of the chalcones differ little from the values of μ for the corresponding thiophene derivatives but are considerably higher than for the furan derivatives. Since all these compounds exist in the same conformational state and the contribution of the intrinsic moment of the heterocycle to the over-all moment of the molecule is insignificant because of its smallness, which is confirmed by the small differences in the calculated values of μ, the high values of μ of the selenophene chalcones as compared with their isologs can be explained by the fact that in the static state the electron-donating influence of the 2-selenienyl group is greater than that of the 2-furyl group but close to that of the 2-thienyl group. This conclusion is also confirmed by investigations of the electronic and vibrational spectra of these compounds [11].

The introduction of substituents differing in their electronic nature into the aromatic nuclei of ketones I and II generally leads to an increase in μ; only in the case of compounds III and XIV, containing F and Cl atoms is the electron moment somewhat smaller. Between the changes in μ under the influence of substituents and the Hammett's σ-constants there is a fairly satisfactory observation of a correlation relationship [5,12] expressed by the formula

$$(\mu_R-\mu_H)/(d_R-d_H)=\rho\sigma,$$

where μ_R is the dipole moment of the ketone having the substituent in the aromatic nucleus; μ_H is the dipole moment of the ketone without a substituent; d_R is the distance from the center of the aromatic nucleus to the center of the charge of the substituent (taken from the literature [12]); d_H is the distance from the center of the aromatic nucleus to hydrogen (2.48 Å) ρ and σ are the constants of Hammett's equation. Fig. 3 shows this correlation for the 1-(2-selenienyl)-3-arylpropen-3-ones.

The anomalously large value of μ appearing for the furan [2] and thiophene [3] chalcones on the introduction of methoxy groups into the ortho positions of the benzene rings has been mentioned previously. A similar phenomenon is observed for the ketones of the selenophene series (see V–X) where the increase in μ is 0.5–0.7 D for each methoxy group. This is possibly connected, on the one hand, with an increase in the nucleophilic nature of the aromatic ring and, as a consequence of this, with an increase in the effect of interaction with the carbonyl group and, on the other hand, with the fact that because of steric hindrance to the free rotation of the methoxy groups arising, the electric moment of the aromatic radical increases. It is an interesting fact that an analogous successive introduction of methoxy groups into the anisole molecule leads to a considerably smaller increase in μ (for anisole, μ is 1.3 D, for 1,3-dimethoxybenzene 1.6 D, and for 1,3,5-trimethoxybenzene 1.8 D [13]).

The table gives the values of μ for the compounds studied calculated by the use of Higashi's empirical equation [14]: $\mu = K\sqrt{\sigma}$, while $K = 0.83$ [15]. In all cases the agreement of the values of μ is fairly good, and the difference between them is in the range ±0.05 D. Only for compounds XVIII and XIX, containing a biphenyl radical, and also for 1,3-di(2-selenienyl)propenone XXIV is the difference somewhat higher, amounting to 0.09 D. This shows the possibility of using Higashi's equation with satisfactory accuracy for the rapid calculation of dipole moments of chalcone analogs.

EXPERIMENTAL

Compounds I–XXIV were obtained by crotonic condensation in an alkaline medium, as described previously [16–18]. The dipole moments were measured by Debye's dilute solution method in benzene at 25 ± 0.02° C, as previously [8, 19]. The error of the measurements did not exceed ±0.04 D. The results of the measurements and the calculated figures are given in the table.

REFERENCES

1. S. V. Tsukerman, Yu. N. Surov, and V. F. Lavrushin, ZhOKh, 38, 524, 1968.
2. S. V. Tsukerman, A. I. Artemenko, and V. F. Lavrushin, ZhOKh, 34, 3591, 1964.
3. S. V. Tsukerman, V. M. Nikitchenko, V. D. Orlov, and V. F. Lavrushin, KhGS, [Chemistry of Heterocyclic Compounds], 3, 232, 1967.
4. S. V. Tsukerman, V. P. Izvekov, and V. F. Lavrushin, 42, 2159, 1968.

5. S. V. Tsukerman, Chan Kuoc Shon, and V. F. Lavrushin, ZhFKh, 40, 160, 1966.
6. H. V. Robles, Rec. trav. chim., 58, [111], 1939.
7. B. Tamamusi, H. Akiyama, and S. Umezawa, Bull. Chem. Soc. Japan, 14, 310, 1939; C. A, 33, 9064^3, 1939.
8. S. V. Tsukerman, V. D. Orlov, and V. F. Lavrushin, ZhSKh, 10, 263, 1969.
9. M. Mario, F. Giovanna, and G. Giulia, Acta Crystallogr., 15, 737, 1962.
10. S. V. Tsukerman, V. D. Orlov, Yu. S. Rozum, and V. F. Lavrushin, KhGS [Chemistry of Heterocyclic Compounds], 5, 980, 1969.
11. S. V. Tsukerman, V. D. Orlov, V. M. Nikitchenko, Yu. S. Rozum, V. F. Lavrushin, and Yu. K. Yur'ev, TEKh, [Theoretical and Experimental Chemistry], 2, 399, 1966.
12. O. Exner, Coll., 25, 642, 735, 1960.
13. O. A. Osipov and V. I. Minkin, Handbook of Dipole Moments [in Russian], Vysshaya shkola, Moscow, 1965.
14. K. Higashi, Bull. Inst. Phys. Chem. Research, Tokyo, 22, 805, 1943; C. A., 43, 7764^a, 1949.
15. K. Bal and K. K. Srivastava, J. Chem. Phys., 27, 835, 1957.
16. S. V. Tsukerman, V. D. Orlov, V. F. Lavrushin, and Yu. K. Yur'ev, ZhOrKh, 1, 650, 1965.
17. S. V. Tsukerman, V. D. Orlov, V. P. Izvekov, V. F. Lavrushin, and Yu. K. Yur'ev, KhGS [Chemistry of Heterocyclic Compounds], 2, 34, 1966.
18. S. V. Tsukerman, V. D. Orlov, V. F. Lavrushin, and Yu. K. Yur'ev, KhGS [Chemistry of Heterocyclic Compounds], 2, 913, 1966.
19. S. V. Tsukerman, V. D. Orlov, Yu. N. Surov, and V. F. Lavrushin, ZhSKh, 9, 67, 1968.

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