# Conclusions

1. A normal coordinate analysis confirms the experimental data, according to which in 2-thia-2-dimethylamino-1,3,2-dioxaphosphorinane there exists an equilibrium between two chair forms with an axial and equatorial orientation of the P=S bond.

2. For a cis-4-Me-substituted heterocycle, the calculation indicates the existence of a single structure, a chair form with an axial P=S bond, and for the trans-isomer, a three-component equilibrium of two chair forms and one boat form.

#### LITERATURE CITED

- B. A. Arbuzov, R. P. Arshinova, V. N. Nabiullin, A. V. Il'yasov, R. N. Gubaidullin, and T. D. Sorokina, Izv. Akad. Nauk, Ser. Khim., 796 (1983).
- 2. R. R. Shagidullin, I. Kh. Shakirov, A. Kh. Plyamovatyi, and R. P. Arshinova, Izv. Akad. Nauk SSSR, Ser. Khim., 2517 (1984).
- 3. L. A. Gribov and V. A. Dement'ev, Methods and Calculation Algorithms in Theory of Vibrational Spectra of Molecules [in Russian], Nauka, Moscow (1982).
- 4. R. R. Shagidullin and S. A. Katsyuba, Zh. Obshch. Khim., 51, 694 (1984).
- 5. R. R. Shagidullin, I. Kh. Shakirov, R. Kh. Musyakaeva, and I. A. Nuretdinov, Izv. Akad. Nauk SSSR, Ser. Khim., 1890 (1981).
- 6. I. Kh. Shakirov and R. R. Shagidullin, Zh. Obshch. Khim., 48, 508 (1978).

STERIC STRUCTURE OF SOME 1,2-DIARYL-SUBSTITUTED ETHANES

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Polysubstituted ethanes are the classical objects of conformational analysis [1]. The 1,2-diaryl-substituted ethanes were investigated by the methods of IR [2], PMR [3, 4], dipole moments and the Kerr effect [5, 6], and x-ray diffraction [7, 8] as well as by theoretical conformational analysis [4, 9]. However, all the experimental data obtained in the liquid phase only relate to the rotation around the  $C_{sp}^{3-}C_{sp}^{3}$  bond. The rotation of the aromatic rings in these compounds is only known in the solid phase, where the interactions of the crystal lattice determine the structure [7, 8].

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With the object of investigating the conformation with reference to the  $C_{sp}^{3}-C_{sp}^{3}$  and  $C_{aryl}-C_{sp}^{3}$  bonds, the present work considered, with the aid of the complex application of the methods of dipole moments (DMs), the Kerr effect, and atom-atom potential functions (AAPFs), the following compounds



We studied the solutions in CCl. and dioxane. The compounds (IV)-(VII) represent the meso forms. The occurrence of the conformers realized was carried out by the comparison of the experimental values of the DM and the Kerr constant (KC) with the values calculated for the probable steric isomers. The methods for the calculation and measurement of these parameters were described in [10, 11]. The values of the DM and the ellipsoids of polarizability (EPs) of the bonds and groups, which are required for the calculation, were determined for model compounds — the corresponding toluenes:  $\alpha$ -mono- and  $\alpha, \alpha$ -dihalogenotoluenes. Obtaining the

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TABLE 1. Values of the Dipole Moments (m, D) and the Semiaxes of the Ellipsoids of Polarizability ( $b_i$ ,  $A^3$ ) of the Bonds and Groups Utilized in the Calculations [10-12]

Compound		C-	-Ar	C—Y				
	<i>b</i> 4	· b2	<i>b</i> 3	m	$b_L$	<sup>b</sup> T	bV	m
(I)	13.96	12,56	9.02	0.36	_	_		
(ÌI)	19,53	14.71	<b>1</b> 0,31	1,96	-	-	-	-
(III)	18.94	15,72	8,83	4,45	_	-	-	1 -
(IV)	13.76	9,70	6.23	-0.38	3,59	1 1	,99	1.63
(V)	19.96	12,10	8.43	1.22	3.59	1	99	1.63
(ÙI)	12.72	11.41	5.56	-0.40	5.30	2.70		1.65
(ÌIIÍ)	18.92	13.81	7.76	1.20	5.30	2	70	1.65
(ÌIIIÍ)	12.75	11.46	5.48	-0.93	3.36	1.83	(2.21)	1.39
(IX)	13.45	12.16	5.78	0.51	3.56	1.83	(2.21)	1.39
`(X)	18.28	15,27	5.94	3.07	3,36	1.83	(2,21)	1.39

TABLE 2. Conformational Characteristics of the Investigated Compounds

Com- pound	n <sub>T</sub>	n <sub>G</sub>	μ, D	φ <sub>ef</sub> , deg	Com- pound	n <sub>T</sub>	n <sub>G</sub>	μ, D	¢ <sub>ef</sub> , deg
(II) (III) (IV) (V) (V) (VI)	0.6 0.5 0.8 0.5 0.5 0,8	0.4 0.5 0.2 0.5 0.2	2.92 6.64 3.02 2.41 3.07	125 115 130 125 120	(VII) (VIII) (IX) (X)	0.5 0.5 0.5 0.5	0.5 0.5 0.5 0.5	2.42 3.75 1.41 2.76	120 130 130 110

data on these compounds permits the correct consideration of the electronic interactions in the Ar-CXY fragments. The utilized parameters of the polarity and the polarizability are presented in Table 1. The C-H bonds were considered to be isotropic [10], and were not therefore taken into account. The bond angles at C<sub>Sp</sub><sup>3</sup> were taken to be tetrahedral.

There are data on the content of the trans (T) and gauche (G) forms relative to the central C-C bond in dibenzyls [3-5] and 1,2-diaryl-1,1,2,2-tetrachloroethanes [2, 6]. It is virtually the same with some predominance of the T-form. It should be noted that the calculations performed by the method of molecular mechanics, and indicating the predominance of the G-form [4, 9], give rise to doubts [4]. Only qualitative results were obtained by the method of vibrational spectroscopy [2]. The calculation of the values of the occupancy n of the Tand G-conformers were performed by us according to the equation

$$n_T \mu^2 (T) + n_G \mu^2 (G) = \mu_{\exp}^2$$

$$n_T + n_G = 1.$$
(1)

The values obtained are presented in Table 2. For the dibenzyls and their derivatives tetrachloro-substituted at the central bond (1,2-diaryl-1,1,2,2-tetrachloroethanes), the realization of the T- and G-conformers is virtually of equal probability. This is in good accord with the literature data, which indicate the efficiency of the utilization of the system of the group parameters. The dihedral angle in the G-conformation is determined unambiguously. In the compounds of the dibenzyl series, it equals 75° [5]. The theoretical KCs do not describe the experiment at lower values of the angle. In the 1,2-diaryl-1,1,2,2-tetrachloroethanes (VIII)-(X), it is less (60°) due to some pushing apart of the Cl atoms [6]. The lowering of the considered dihedral angle  $C_{ar}$ -C-C- $C_{ar}$  does not lead to steric hindrance since the aromatic rings can unfold and take up a mutual parallel orientation.

The steric structure of the meso-1,2-diaryl-1,2-dihalogenoethanes (IV)-(VII) was not previously studied. It follows from the data presented in Table 2 that the conformational equilibrium is shifted in favor of the T-rotamer for the compounds (IV) and (VI), which are not substituted in a ring. The occupancy of the G-conformations increases for the p-bromo derivatives (V) and (VII). The reason for such a redistribution is evidently in the fact that the introduction of the Br atom into the p-position of the aromatic ring (the Br atom is remote) does not lead to a change of the van der Waals volume of the aromatic group which is sufficient for a shift in the conformational equilibrium, all the more in favor of the G-rotamer with the adjacent halogen atoms and aromatic rings. The dipole moment of the Ar-C group changes direction on the introduction of the Br atom at the p-position, and increases by 1 D; this is

Com- pound		trans Iso- mer (φ, deg)								
	20	40	60	80	100	120	140	160	180	0-180
(I)	9	15	25	35	31,5	12	2	-		19-41
(III)	872	404 1767	2804	3492	3198	345 1333	178	-	-	95-128 87-164
(IV) (V)	-290	$     307 \\     -149   $	481 34	538 189	495	$322 \\ 84$	$127 \\ -92$	-254	-	56-78 166-191
(ŶI) - (VII)	$100 \\ -394$	421 - 158	724 150	838 382	715	$\frac{442}{220}$	107	-110 -342	-106	30-97
(VIII)	479	617	794	854	922	796	619	480	-402	25-97
$(\mathbf{IX})$ $(\mathbf{X})$	530	647	131 833	156 920	163 988	115 843	68 659	51 537		160-270 96-254

TABLE 3. Theoretical KC<sub>ef</sub> of the Investigated Compounds

TABLE 4. Experimental Parameters of the Investigated Compounds

Com- pound	Solvent ,	Δε/Δω2	$\Delta d/d_1\Delta\omega_2$	$\Delta n_D^2 / \Delta w_2$	$\Delta B/B_1 \Delta \omega_2$	μ, D	m <sup>K · 10<sup>12</sup>, esu</sup>
(I) (III) (III) (IV) (V) (VI) (VII) (VIII) (IX) (X)	$\begin{array}{c} \mathrm{CCl}_4\\ \mathrm{CCl}_4\\ \mathrm{dioxane}\\ \mathrm{CCl}_4\\ \mathrm{dioxane}\\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ &$	$\begin{array}{c} 0.732\\ 2.296\\ 10.131\\ 1.781\\ 0.460\\ 1.010\\ 1.378\\ 5.043\\ 1.033\\ 1.643\end{array}$	$\begin{array}{c} 0.150\\ -0.043\\ -0.020\\ -0.033\\ -0.150\\ -0.943\\ -0.104\\ -0.072\\ -0.036\\ -0.105\end{array}$	$\begin{array}{c} 0.579\\ 0.319\\ 0.518\\ 0.498\\ -0.430\\ 0.395\\ 0.511\\ 0.358\\ 0.461\\ 0.519\end{array}$	$\begin{array}{c} 20.09\\ 69.37\\ 216.72\\ 53.57\\ 18.59\\ 31.45\\ 25.81\\ 159.84\\ 27.70\\ 113.43\end{array}$	0.33 1.83 4.58 1.28 1.75 1.25 1.81 2.64 1.00 1.88	$\begin{array}{c} 28\\ 168\\ 672\\ 102\\ 90\\ 129\\ 150\\ 386\\ 76\\ 536\end{array}$

an indication of the change in the electronic structure of the ArCHHal fragments which is probably responsible for the observed shift of the conformational equilibrium.

The angle of rotation of the plane of the aromatic ring around the  $C_{ar}$ -C bond may be different in the T- and G-rotamers. On the rotation of one of the rings by the angle  $\phi^{\scriptscriptstyle +}$  the possible rotation of the second ring both by the angle  $\phi^+$  and by  $\phi^- = 180 - \phi^+$  should be considered. The method of electrical double refraction is very informative in the investigation of the structure of aromatic compounds. One of the basic parameters of the method of the KC depends on the orientation of the  $\pi$ -electron cloud of the ring; this permits the determination of the angle of rotation of this fragment relative to the other bonds and groups. However, this is impossible when the vector of the molecular dipole moment, the direction of the maximal polarizability of the rotating groups, and its axis of rotation coincide. In this case, the molecular KC is virtually independent of the rotation of the group. In fact, the value of the KC for the T-conformation of 1,2-diaryl-substituted ethanes, in which the described conditions apply, in all the investigated compounds changes less on average than for the G-conformer with the 180° rotation of the aromatic rings (Table 3). Therefore, the method of electrical double refraction is not sensitive to the rotation of the aromatic rings in the T-conformer in the case of 1,2-diaryl-substituted ethanes; this simplifies the determination of the conformational problem by the consideration of the mutual orientation of the bonds and groups only in the G-conformer. It was proposed by us that the angles of the rotation of both the aromatic rings  $\phi_1$  and  $\phi_2$  relative to the central C-C bond are the same. On consideration of the Newman projection from the side of the p-substituent, the rotation of the hour hand was regarded as positive. The possibility of the realization of two nonidentical G-conformers, differing in the mutual orientation of the rings -  $G(\phi_1^+\phi_2^+) \equiv G(\phi_1^+\phi_2^-)$  was noted above. Here, the lower index is the conditional numeration of the rings; the upper index is the direction of the rotation. The mutual orientation of the rings, i.e., the values n++ and n+of the occupancy of the two G-conformations noted, is mainly determined by the non-valent interactions of the atoms. After the calculation of the molecular energies as functions of the  $\phi_1$  and  $\phi_2$  angles in the framework of the additive model of interatomic interactions, we found the values of occupancy by the equation over the whole interval of change of the angles (0-180°)

$$n^{++}/n^{+-} = \exp\left(-\Delta E/RT\right) \tag{2}$$







Fig. 2. The graph of the dependence of  $K_{\rm G}^{\rm ef}$  on the angle of rotation in  $C_6H_5CCl_2-C_6H_5$  (VIII),  $FC_6H_4CCl_2-CCl_2C_6H_4F$  (IX), and  $O_2NC_6H_4CCl_2-CCl_2-C_6H_4NO_2$  (X).

We performed the calculation of the energies by the MAP-3 program. The potentials of the non-valent interactions of Dashevskii [13] and the standard lengths of the bonds and bond angles [14] were utilized. The barrier to the rotation around the  $C_{ar}$ -C bond was assumed to be zero just as in toluene [15]. The geometry was not optimized. One of the conformational maps constructed is presented in Fig. 1.

The values of the KC of the conformations  $G\left(\phi_1^+\phi_2^+\right)$  and  $G\left(\phi_1^+\phi_2^-\right)$  were calculated for all the compounds considered. Further, the effective molecular KCs (mK) of the G-conformers of the compounds (I)-(X) were calculated by the equation (3) taking into account the corresponding occupancy values

$${}_{m}K_{G}^{\text{ef}} = n^{++} {}_{m}K_{G}^{++} + n^{+-}{}_{m}K_{G}^{+-}$$
(3)

In the end, the value of  ${}_{m}K_{G}{}^{ef}$  is a function of the effective angle of rotation  $\varphi$  of the aromatic rings. If this dependence is presented in the form of a graph with the appropriate coordinates, then intersecting it with the line corresponding to the experimental value of the KC of the G conformer will permit the determination of the value of  $\varphi$ . According to the rule of the additivity of the mixtures, which was already utilized, the experimental KC of the 1,2-diaryl-substituted ethanes is described as follows:

$${}_{m}K_{\text{exp}} = n_{Tm}K_{T} + n_{Gm}K_{G} \tag{4}$$

where  ${}_{m}K_{G}$  is the desired KC of the G-conformer;  ${}_{n_{T}}$  and  ${}_{n_{G}}$  are occupancy values of the T- and G-conformers determined by the method of DMs. It was noted above that the KC of the T-conformer only shows a dependence on the angle  $\phi$  in a narrow interval which is limited, in the general case, by the values of  ${}_{m}K_{T}{}^{min}$  and  ${}_{m}K_{T}{}^{max}$ . On the basis of the data obtained for the compounds (II)-(X), the graphical dependences of  ${}_{m}K_{G}{}^{ef}$  on the angle of rotation  $\phi$  were constructed. Examples of the graphs are presented in Fig. 2. On the one hand, the crosshatched regions represent the "limited" values of  ${}_{m}K_{G}$ , calculated according to the equation

$${}_{m}K_{G}^{\min} = ({}_{m}K \exp - {}_{m}K_{T}^{\min} n_{T})/n_{G}$$

$${}_{m}K_{G}^{\max} = ({}_{m}K \exp - {}_{m}K_{T}^{\max} n_{T})/n_{G}$$
(5)

On the other hand, they represent the region of the possible intervals of the values of the effective angle of rotation  $\phi$  of the rings. In the general case, it does not exceed 20°, so that the values of  $\phi_{ef}$  presented in Table 2, which are determined graphically, are the mean values of the interval  $\phi \pm 40^{\circ}$ .

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The calculations of the orientation of the aromatic rings in the G-conformation of the compounds (IV)-(X) by the method of molecular mechanics, according to the model of the additive interatomic interactions, showed only one entire minimum ( $\varphi_1 = 100^\circ, \varphi_2 = 80^\circ$ ). For the compounds (I)-(III), it corresponds with the values of the angles  $\varphi_1 = 100^\circ$ ,  $\varphi_2 = 100^\circ$ . This is only the result of the calculation of the steric interactions of the atoms of the two aromatic rings, rotating relative to each other and relative to the atoms of the main chain. The drawing from the data on the polarities and polarizabilities of the bonds and groups permitted the specification of the values of the angles. It follows from the values of  $\phi_{ef}$  presented in Table 2 that the rings are oriented mutually in parallel, and are turned by the average angle of 120 ± 10° in relation to the central C-C bond, i.e., they virtually shield the C-H bonds. The results of the x-ray structural investigation of the di- [7] and tetraphenyl-substituted [8] ethanes confirm the approximate parallel disposition of the aromatic groups in pairs. Their orientation relative to the C-C bond is close to the orthogonal.

Therefore, the results obtained are entirely in accordance with the general conformational tendency of the mono, di, and tri- $\alpha$ -halogeno-substituted toluenes [12] and the data for the 1,2-diaryl-substituted ethanes [2-8].

### Experimental

Compound (I) is an industrial sample. The remaining compounds were synthesized by known methods. Compound (II) was synthesized by the reaction of dibenzyl with bromine vapor. Compound (III) was synthesized by the action of HNO3 on dibenzyl. The meso-1,2-diphenyl-1,2-dichloro- and dibromoethanes (IV)-(VII) were synthesized by the action of the mixture of  $SO_2Cl_2$ and PCl3 on the corresponding 1,2-diphenylethanes with UV exposure, or the action of Br2 in CC14. The 1,1,2,2-tetrachlorodiphenylethanes (VIII)-(X) were synthesized from the corresponding benzotrihalogenides by boiling them in pyridine with copper powder. The products were purified by recrystallization until the physical constants matched those presented in [16]. The DMs and the KCs were determined according to [10] in CC14 and dioxane at 25°C. The experimental parameters of the compounds investigated are given in Table 4.

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## Conclusions

In the investigated 1,2-diaryl-substituted ethanes, the content of the trans and gauche conformers relative to the C-C bond is practically identical; the trans form shows some predominance. In these compounds, the aromatic rings are orientated in parallel and are turned by an average of  $120 \pm 10^{\circ}$  relative to the central C-C bond.

#### LITERATURE CITED

- 1. W. J. Orville-Thomas (ed.), Internal Rotation in Molecules Wiley (1974).
- 2. M. E. Chin, B. C. Giebert, and P. Hanson, J. Chem. Soc. B, 1645 (1970).
- 3. A. J. M. Reuvers, A. Sinnema, F. van Rantwijk, J. D. Kemijnse, and H. van Bekkum, Tetrahedron, 25, 4455 (1969).
- 4. J. Jacobus, Tetrahedron Lett., 2927 (1976).
- 5. K. K. Chin, H. H. Huang, and L. H. L. Chia, J. Chem. Soc. Perkin Trans. 2, 286 (1972).
- 6. L. H. L. Chia, K. K. Chin, and H. H. Huang, J. Chem. Soc. B, 1117 (1969).
- 7. C. M. Weeks, S. Pokrywieski, and W. L. Duax, Acta Crystallogr., <u>B29</u>, 1729 (1973).
- 8. D. A. Dougherty, K. Mislow, J. F. Blount, J. B. Wooten, and J. Jacobus, J. Am. Chem. Soc., 99, 6149 (1977).
- 9. P. Ivanov, I. Poyazlieff, and N. Tyutulkov, Tetrahedron Lett., 775 (1976).
- 10. A. N. Vereshchagin, The Polarizability of Molecules [in Russian], Nauka, Moscow (1980), p. 177.
- 11. O. A. Osipov, V. I. Minkin, and A. D. Garnovskii, Handbook on Dipole Moments [in Russian], Vyssh. Shk., Moscow (1977), p. 257.

- 12. I. M. Khamatullina, Dissertation, Kazan' (1977).
- V. G. Dashevskii, Conformational Analysis of Organic Molecules [in Russian], Khimiya, Moscow (1982), p. 271.
- 14. A. J. Gordon and R. A. Ford, A Chemist's Companion, Wiley (1973).
- 15. J. P. Lowe, in: Progress in Physical-Organic Chemistry, Vol. 6, Interscience, New York (1968), pp. 1-80.
- 16. Beilsteins Handbuch der Organischen Chemie, Vol. 5, Berlin (1956), p. 1809.

MAGNETOELECTRIC PROPERTIES AND CONFORMATIONAL ANALYSIS OF

#### α, β-DIHALOETHYLBENZENES

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The presence of several axes of internal rotation in the molecules of  $\alpha$ , $\beta$ -dihaloethylbenzenes accounts for their conformational variability. As a result of rotation around the ethane bond, the appearance (without consideration of optical isomerism) of three energetically different rotamers with trans orientations of the C-Hal bonds relative to one another and two rotamers with gauche orientations of these bonds is possible. In the ideal cases, they have the dihedral torsion angles  $\Psi = 180^{\circ}$  (T) and  $60^{\circ}$  (G<sub>1</sub> and G<sub>2</sub>), respectively (Fig. 1). In reality, deviations from the canonical staggered structures are possible. In addition, in each of the rotamers the spatial orientation of the plane of the aryl radical relative to the  $\alpha$ substituents may be different (see Fig. 1).

Thus, the problem of the structure of these molecules is defined by nine conformational

parameters, three of which  $(n_T, n_{G_1}, n_{G_2})$  together with the normalization condition  $\sum_{i=1,2,3,n} n_i = 1$ 

describe the composition of the equilibrium mixture, while the six others represent the torsion angles  $\Psi_{\mathbf{i}}$  and the dihedral angles of rotation of the planes of the aryl group  $\varphi_T$ ,  $\varphi_{G_1}$ , and  $\varphi_{G_2}$ . The solution of this many-parameter problem clearly requires the use of a large set of physical methods, the utilization of data from theoretical conformational analysis, and examination of the properties of isoconformation compounds.

In the present work we carried out a conformational analysis of  $\alpha$ , $\beta$ -dichloroethylbenzene,  $\alpha$ , $\beta$ -dibromoethylbenzene, and their p-chloro derivatives with the general formula XC<sub>6</sub>H<sub>4</sub>CHHal-CH<sub>2</sub>Hal, where X = H, Hal = Cl (I); X = Hal = Cl (II); X = H, Hal = Br (III); X = Cl, Hal = Br (IV), dissolved in CCl<sub>4</sub>.

Since the relative orientation of the highly polar vicinal C-Hal bonds in two rotameters is different, we carried out measurements of the dipole moments (DM's) in order to establish the conformational composition. The effects of the electric and magnetic birefringence (the



Fig. 1. Possible conformations of the  $\alpha,\beta$ -dihaloethylbenzenes studied (I-IV).

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