CONFORMATION OF UNSYMMETRICAL DIARYL DISULFIDES

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When studying the problem of transmitting intramolecular interactions through a dielement bond E—E (where E = chalcogen), valuable information can be obtained from a study of the physicochemical properties of unsymmetrical compounds R'—E—E—R", in which the R' and R" groups have a different electronic character.

In the present paper the methods of dipole moments (DM), Kerr effect, and Rayleigh light scattering were used to study the spatial structure of some unsymmetrical diaryl disulfides:

$$p\text{-}XC_6H_4\text{—}S\text{—}S\text{—}C_6H_4Y\text{-}p' \quad (Y = NO_2;\ X = CH_3\ (I),\ H\ (II),\ Br\ (III),$$
$$Cl\ (IV),\ F\ (V);\ Y = Cl;\ X = CH_3O\ (VI),\ CH_3\ (VII),\ H\ (VIII))$$

The obtained results are compared with the conformation picture in the series of the corresponding symmetrical diaryl disulfides [1].

The experimental values of the DM (μ_{expt}), molar Kerr constants (KC) $_\infty({}_mK_2)$, molecular polarizabilities (b), exaltations of the polarizability (Δb), and anisotropies of the molecular polarizability $_\infty\delta_2{}^2$ of the discussed compounds are given in Table 1. The effective conformations of the molecules were determined the same as in [1]. When calculating the theoretical KC values it was assumed that molecules (I)-(VIII) have a skewed conformation. The value of the dihedral angle Φ between the planes of the C_{ap}—S—S and C_{ap}'—S—S bonds in the disulfide molecules with regular p-substituents was calculated using the equation

$$\cos\Phi = \frac{\mu^2_{\text{expt}} - (m_1{}^2 + m_2{}^2)\cos^2(\delta - 90°) - (m_1 \pm m_2)^2 \sin(\delta - 90°)}{\mp 2m_1m_2\cos^2(\delta - 90°)}$$

where μ_{expt} is the experimental DM value of the discussed disulfide, m_1 and m_2 are, respectively, the moments of the $p\text{-}YC_6H_4S$ and $p\text{-}XC_6H_4S$ fragments, and δ is the C—S—S valence angle (106°). The upper sign is taken for compounds (I), (II), (VII), and (VIII), and the lower sign is taken for (III)-(V).

From the data given in Table 1 it can be seen that for the studied diaryl disulfides, Φ ~ 80°. For compounds (III)-(V), in view of the substantial resonance interaction between the p-substituents of the benzene rings that is possible in them, which cannot be taken into account when the calculations are made by the additive scheme, the found values of the Φ angles (respectively, 134, 118, and 125°) must be considered to be unreliable. Consequently, when calculating the ${}_mK_{\text{theor}}$ for these compounds it was assumed that Φ = 80°. For (VI) the Φ angle was also taken equal to 80°, the same as for the disulfides with regular p-substituents.

The polarizability tensors of the individual bonds and groups of atoms were taken from [1, 2]. An exaltation of the polarizability Δb was observed for most of the compounds (see Table 1), which in the case of (I)-(V) was taken into account as a correction along the 1,4 axis of the $p\text{-}O_2NC_6H_4$ fragment; in (VI) and (VII) the exaltation of the polarizability was taken into account by introducing the correction Δb/2 along the 1,4 axis of both benzene rings.

The found values of ψ and ξ, which respectively characterize the rotation of the $p\text{-}YC_6H_4$ and $p\text{-}XC_6H_4$ fragments around the C_{arom}—S bonds, are given in Table 1. As can be seen, the deviation of the $p\text{-}O_2NC_6H_4$ fragment from the plane of the C—S—S bonds in (I)-(III) is ∿ 15°, a value that is close to the value in the symmetrical $(p\text{-}O_2NC_6H_4)_2S_2$ derivative [1].

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TABLE 1

Compound	Substituent		b_{calc}	b_{expt}	Δb	μ expt, D	$_\infty m K_2 \cdot 10^{12}$	$_\infty \delta_2^2 \cdot 10^3$	φ°	ψ°	ξ°
	Y	X	Å³								
(I)	NO_2	CH_3	90,0	96,2	6,2	3,91	1901	40,93	77	15	75
(II)	NO_2	H	83,9	86,8	2,9	3,72	1512	30,16	70	10	65
(III)	NO_2	Br	95,7	93,4	2,3	3,23	1482	30,44	(80)	15	85
(IV)	NO_2	Cl	96,3	90,3	6,0	3,05	2368	47,78	(80)	—	—
(V)	NO_2	F	89,8	84,3	5,5	3,19	2346	55,39	(80)	—	—
(VI)	Cl	CH_3O	93,0	91,7	1,3	2,39	315	27,56	80	67	83
(VII)	Cl	CH_3	90,2	89,6	0,6	1,86	159	20,87	82	64	46
(VIII)	Cl	H	83,7	83,7	0,0	1,38	99	13,89	84	55—65	35—45

TABLE 2

Compound	mp, °C bp, °C (p, mm of Hg)	Found, %				Calculated, %			
		C	H	S	Hal	C	H	S	Hal
(III)	98–99	42,09	2,37	18,95	23,38	42,04	2,35	18,87	23,31
(V)	59–60	51,44	3,10	–	–	51,13	2,86	–	–
(VI)	167 (0,05)	54,84	4,11	22,91	12,68	55,10	3,91	22,82	12,51
(VII)	54–55	58,39	4,00	24,36	13,49	58,40	4,14	24,18	13,26
(VIII)	147 (0,09)	56,95	3,78	25,44	14,08	56,89	3,38	25,52	13,99

As regards the second aromatic p-XC_6H_4 fragment in (I)-(III), then its emergence from the plane of the C'—S—S bonds, characterized by the angle ξ = 65-85°, increases when compared with the symmetrical disulfides [1].

In (VI)-(VIII) an increase of ~25-30° is observed in the angles of rotation around the C—S bonds of the p-XC_6H_4 and p-YC_6H_4 fragments when compared with the corresponding symmetrical disulfides [1].

The obtained data are in agreement with the postulation expressed in [1, 2] that an interrelationship exists between the conformations of aromatic disulfides and the electronic character of the p-substituents of benzene rings, and that the electronic effects can be transmitted through the disulfide bridge. The results of studying compounds (IV) and (V) also testify in support of such a postulation. A very substantial redistribution of the axes of the molecular polarizability ellipsoid apparently occurs in the molecules of these compounds, which, with the usual values of b_i, does not permit obtaining for them a correct idea as to the true value of $_mK_{theor}$ and determination of the conformation. Thus, for example, for (IV) the maximum calculated value of $_mK_{theor}$, equal to 1917 when $\psi = \xi = 90°$, is substantially smaller than the experimental value (see Table 1). A similar picture is also observed for (V). A change in the polarizability anisotropy of the p-$O_2NC_6H_4$ fragment was established on the example of p-nitroanisole [3]. We calculated $_mK_{theor}$ for (IV) and (V) using for p-$O_2NC_6H_4$ the value of the polarizability tensor found in [3]. However, agreement between $_mK_{theor}$ and $_mK_{expt}$ was also not achieved in this case. This result is apparently caused by the existence of strong resonance interaction between the p-substituents of adjacent benzene rings in the discussed compounds through the π-aromatic system and dielement bond.

EXPERIMENTAL

Compounds (I) and (II) were obtained as described in [4]; (III) and (V)-(VIII) were synthesized by reacting p-YC_6H_4SCl (Y = NO_2, Cl) with the appropriate thiophenol in dry CCl_4 as described in [5]. Compound (IV) was synthesized as described in [6], by mixing CCl_4 solutions of p-$O_2NC_6H_4SCl$ and p-$ClC_6H_4HgSC_6H_5$. The compounds were purified immediately before the measurements either by repeated recrystallization or fractional distillation in vacuo. Their composition and purity were confirmed by the elemental analysis and the TLC on Silufol, and also by agreement of their physical constants with the literature data. The properties of the new compounds are given in Table 2.

The DM were determined using the method of dilute Debye solutions. The KC were determined as described in [7], while the degree of depolarization of the scattered light was determined as described in [8]. All of the measurements were run in CCl_4 solution at 25 ± 0.1°C.

CONCLUSIONS

1. In solution the unsymmetrical p-substituted diaryl disulfides have a skewed conformation with a dihedral angle of ~80°.

2. The angles of rotation of the aryl fragments relative to the planes of the C_{ar}—S—S bonds in the molecules of different compounds depend on the nature of the p-substituents.

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CYCLOADDITION OF DIAZOACETIC ESTER TO 16-DEHYDROPREGNENOLONE ACETATE UNDER HIGH PRESSURE

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It is known that certain bimolecular reactions, which are characterized by a high negative bulk activation effect and proceed in low yields at atmospheric pressure, are accelerated by high pressure [1]. It was recently shown by us that the cycloaddition of labile nitronic esters to 16-dehydro-20-keto steroids, which proceeds at atmospheric pressure in a yield of ~1%, gives high yields of the cycloadducts at 14,000 atm [2].

The present communication is devoted to studying the effect of high pressure on the cycloaddition of diazo compounds. Ethyl diazoacetate (EDA) and 16-dehydropregnenolone acetate (I) were selected as the study objects. It should be mentioned that the thermal (120°C) addition of EDA to (I) was described previously, which leads to a single product, namely the Δ^2-pyrazoline (III). The isomeric Δ^1-pyrazoline (II), which typifies the usually observed cycloadducts when diazoalkanes are used, was not detected [3]. Examples are also known of the exclusive formation of Δ^2-carbethoxypyrazolines in the series of nonsteroidal dipolarophiles [4]. It may be assumed that pyrazoline (III) is a secondary reaction product and the shift of the double bond in the initially formed Δ^1-pyrazoline (II) is related to the drastic reaction conditions. Then the transition from thermal acceleration of the cycloaddition reaction to acceleration by pressure could prevent this isomerization.

Actually, the addition of EDA to 16-dehydropregnenolone acetate (I) at 20° under a pressure of 14,000 atm leads in an overall yield of 75% to two isomeric steroido[16α,17α]pyrazolines (II) and (III) in a 3:2 ratio. The ratio of the isomers was established by analyzing the reaction mixture by NMR. The fast chromatographic separation of the mixed reaction products in a nitrogen atomosphere made it possible to isolate the pure (II) and (III) in approximately the same ratio.

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