Dipole Moments of Some Diaryl Disulfides

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The dipole moments data of diphenyl disulfide and its o-amino, o-nitro, o-acetyl, o-diacetyl, 5-chloro-2-amino, and 4-chloro-2-nitro symmetric disubstituted derivatives, at 25° and 45°C in benzene solution, are reported. The μ values found support a previously postulated rigid "skew" configuration.

Since the conformational concepts about the disulfide group are becoming increasingly important in determining the protein structure, the stereochemistry of the S—S group has been extensively investigated using X-ray and other physical methods.

Previous determinations of the electric dipole moment of dialkyl and diaryl disulfides are reported in the literature (*1, 2, 4, 7, 9, 10, 13, 15, 17, 21, 24, 26, 27*), but they are limited, up to date, to not very many cases of diaryl disulfides, and no data are given on the temperature dependence.

The present work reports measurements on some symmetrically substituted derivatives of diphenyl disulfide at 25° and 45°C in benzene solution, providing additional experimental information on model disulfide systems.

None of the compounds examined previously has been investigated, except diphenyl disulfide.

EXPERIMENTAL

Materials. The diphenyl disulfide (I), bis(o-aminophenyl)-disulfide (II), bis(o-nitrophenyl)disulfide (III), and bis(4-chloro-2-nitrophenyl)disulfide (IV), commercial Eastman Kodak Co. products, were purified following well-known methods (*5, 16, 22*). The bis(o-acetylaminophenyl)disulfide (V), bis(o-diacetylaminophenyl)disulfide (VI), and bis(5-chloro-2-aminophenyl)disulfide (VII) were synthesized according to the literature (*3, 6, 18*).

Each compound was extensively recrystallized, immediately before its dipole moment was determined, to a constant melting point and heated in vacuo (less than 1 torr) overnight over P_2O_5 at temperatures below its melting point. For the assessment of purity, a Perkin-Elmer differential scanning calorimeter Model DSC-1B was used. The operating conditions of the instrument were at maximum sensitivity with heating rate 0.625°/min in a continuous (1 ml/min) stream of N_2. The thermal lag was measured with a calibration compound (NBS and Fisher) melting near each sample. The purities calculated by this method (*20, 25*) were greater than 99.96% for all the compounds.

Thiophene-free benzene, used as solvent, was stored and refluxed over sodium and then distilled shortly before use. The following solvent constants apply at 25°C: $\epsilon = 2.2725$; $v = 1.14445$; $n_D = 1.49790$; with temperature coefficients (*23*) $d\epsilon/dt = -0.0020$; $dv/dt = 0.00136$; $dn_D/dt = 0.00064$.

Apparatus and Method. A Dekameter WTW, DM 01 Type, was used for the dielectric constant measurements. The dielectric cell was calibrated, at the selected temperatures, with air and with standard liquids (*14*).

The refractive indexes were measured, reading to ±0.00001, respect to the Na_D line on a Bausch & Lomb precision refractometer of modified Abbe type, which had been calibrated with 1-bromonaphthalene and anise oil as refractometric standards.

The specific volumes were determined on an Ostwald-type pycnometer of about 10-cc capacity: The weight of solution filling the pycnometer was reproducible to 0.1 mg.

The temperature of experience was regulated within ±0.01°C by a Lauda NB-S ultrathermostat and was controlled with a mercury thermometer (calibrated precision against an NBS certified standard) using the fixed points of the International Temperature Scale.

The total solute polarization was obtained by extrapolation at infinite dilution ($P_{2\infty}$) with the Halverstadt and Kumler method (*11*). By this method solvent polarization error is essentially eliminated by plotting, for a series of solutions, the dielectric constant ϵ_{12} and the specific volume v_{12} vs. the weight fraction w_2 of solute and extrapolating to $w_2 = 0$: The constants of the straight line equation give the values ϵ_{10}, α, v_{10}, and β necessary to calculate $P_{2\infty}$.

The electronic and atomic polarization, P_e and P_a, was taken to be equal to the distortion polarization assumed as 1.05 R_D, where R_D is the observed molar refraction (constant at the two temperatures), and then the dipole moments values were calculated from the usual Debye equation.

The Guggenheim procedure (*8*) also gave the same results.

The Hoecker plot (*12*) indicated that no association of the disulfides was existing in the range of concentrations used.

The probable error in μ is estimated to range from ±0.01 to ±0.02 *D* at 25°C and from ±0.02 to ±0.03 *D* at 45°C. Duplicate determinations of the electric moment showed a reproducibility greater than ±0.02 *D*.

RESULTS AND DISCUSSION

Table I gives the experimental data. The μ values, expressed in Debye units, and the parameters for their evaluation obtained by the least-squares method are summarized in Table II.

The near constancy of the moment with change in temperature found for the compounds examined confirms a previously described rigid configuration for diphenyl disulfide, bis(p-chlorophenyl)disulfide and di-β-naphthyldisulfide: Aroney et al. (*1, 2*) have shown, by dipole moment, molar Kerr constant, and dielectric relaxation data that rotation about the S—S bond is greatly hindered and the preferred conformations are nonplanar, skewed, with possible torsional oscillations of the phenyl groups about the C—S bonds.

A solution conformation study recently carried out (*19*) for bis(o-nitrophenyl)disulfide (III) gives further support to this model.

Interpretation of the difference in μ at the two temperatures for the derivatives III and IV appears to be complicated by additional modes of intramolecular rotation owing to the substituent groups present.

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Table I. Weight Fractions of Solute, Dielectric Constants, Specific Volumes and Refractive Indexes of Solutions in Benzene

25°C				45°C			
$100\ w_2$	ϵ_{12}	v_{12}	n_{12}	$100\ w_2$	ϵ_{12}	v_{12}	n_{12}
Diphenyl disulfide (I)							
0.4055	2.2804	1.14149	1.49819	0.4488	2.2443	1.16660	1.48558
0.4961	2.2824	1.14123	1.49830	0.5967	2.2472	1.16615	1.48575
0.5341	2.2832	1.14111	1.49836	0.6570	2.2483	1.16586	1.48587
0.6121	2.2848	1.14086	1.49847	0.7466	0.2500	1.16559	1.48598
0.7043	2.2865	1.14056	1.49858	0.8252	2.2514	1.16541	1.48604
0.8394	2.2893	1.14012	1.49875	0.9399	2.2536	1.16499	1.48621
Bis(*o*-aminophenyl)disulfide (II)							
0.3492	2.2817	1.13938	1.49828	0.5802	2.2505	1.16522	1.48591
0.4374	2.2844	1.13894	1.49863	0.6085	2.2515	1.16507	1.48596
0.4892	2.2860	1.13859	1.49853	0.7189	2.2545	1.16452	1.48615
0.6211	2.2894	1.13805	1.49875	0.8308	2.2573	1.16387	1.48637
0.6762	2.2910	1.13734	1.49887	0.8491	2.2579	1.16370	1.48649
0.9183	2.2986	1.13686	1.49926	1.1270	2.2653	1.16230	1.48690
Bis(*o*-nitrophenyl)disulfide (III)							
0.2001	2.2937	1.14161	1.49802	0.1044	2.2449	1.16773	1.48509
0.3847	2.3132	1.14079	1.49825	0.1586	2.2496	1.16741	1.48518
0.4439	2.3190	1.14052	1.49837	0.2362	2.2582	1.16696	1.48533
0.5689	2.3325	1.13996	1.49853	0.2686	2.2596	1.16677	1.48536
0.6999	2.3460	1.13937	1.49870	0.3646	2.2695	1.16621	1.48552
0.7965	2.3563	1.13893	1.49887	0.4543	2.2785	1.16569	1.48567
Bis(4-chloro-2-nitrophenyl)disulfide (IV)							
0.2022	2.2801	1.14174	1.49784	0.1990	2.2425	1.16728	1.48504
0.2692	2.2826	1.14122	1.49797	0.2412	2.2441	1.16689	1.48516
0.2926	2.2834	1.14104	1.49802	0.2824	2.2456	1.16652	1.48527
0.3359	2.2850	1.14071	1.49813	0.3284	2.2474	1.16608	1.48541
0.3846	2.2874	1.14037	1.49824	0.3535	2.2483	1.16587	1.48547
0.4015	2.2866	1.14021	1.49820	0.4162	2.2506	1.16528	1.48524
Bis(*o*-acetylaminophenyl)disulfide (V)							
0.2733	2.2832	1.14162	1.49795	0.1726	2.2415	1.16758	1.48506
0.3096	2.2847	1.14146	1.49802	0.2390	2.2441	1.16729	1.48518
0.3180	2.2850	1.14142	1.49802	0.2612	2.2449	1.16716	1.48521
0.3648	2.2867	1.14120	1.49808	0.3051	2.2465	1.16697	1.48529
0.3759	2.2872	1.14116	1.49813	0.3624	2.2487	1.16669	1.48540
0.4264	2.2892	1.14092	1.49819	0.4012	2.2502	1.16652	1.48547
Bis(*o*-diacetylaminophenyl)disulfide (VI)							
0.4918	2.2920	1.14040	1.49802	0.4633	2.2527	1.16581	1.48541
0.7456	2.3019	1.13943	1.49824	0.7137	2.2622	1.16482	1.48564
0.9651	2.3103	1.13853	1.49847	0.8647	2.2682	1.16425	1.48575
1.1897	2.3194	1.13773	1.49858	1.0382	2.2747	1.16363	1.48592
1.4521	2.3292	1.13672	1.49883	1.0938	2.2764	1.16344	1.48598
1.5544	2.3330	1.13628	1.49892	1.4562	2.2903	1.16207	1.48629
Bis(5-chloro-2-aminophenyl)disulfide (VII)							
0.2555	2.2845	1.14153	1.49809	0.4056	2.2538	1.16590	1.48557
0.3591	2.2899	1.14098	1.49823	0.5003	2.2578	1.16536	1.48575
0.4773	2.2962	1.14036	1.49841	0.5605	2.2616	1.16501	1.48586
0.6051	2.3026	1.13970	1.49853	0.6566	2.2657	1.16446	1.48597
0.8642	2.3163	1.13834	1.49892	0.8644	2.2753	1.16327	1.48638
1.1230	2.3296	1.13697	1.49925	1.0832	2.2857	1.16201	1.48674

Table II. Total Polarizations (cc), Molar Refractions (cc), Dipole Moments (D), and Other Parameters for Their Evaluation

	Disulfide	Temp	α	ϵ_{10}	β	v_{10}	$P_{2\infty}$	R_D	μ
(I)	Diphenyl (mp 61–2°C) (*22*)	25	2.03	2.2723	−0.323	1.14283	136.78	69.1	1.77
		45	1.91	2.2357	−0.325	1.16805	136.05	69.1	1.81
(II)	Bis(*o*-aminophenyl) (mp 93–4°C) (*16*)	25	2.92	2.2714	−0.497	1.14111	183.69	71.2	2.30
		45	2.69	2.2350	−0.538	1.16834	176.21	71.2	2.29
(III)	Bis(*o*-nitrophenyl) (mp 194–5°C) (*5*)	25	10.48	2.2727	−0.449	1.14251	671.66	86.1	5.32
		45	9.59	2.2346	−0.582	1.16833	630.86	86.1	5.30
(IV)	Bis(4-chloro-2-nitrophenyl) (mp 212–3°C) (*5*)	25	3.69	2.2725	−0.767	1.14329	304.27	88.4	3.21
		45	3.71	2.2351	−0.920	1.16911	301.06	88.4	3.29
(V)	Bis(*o*-acetylaminophenyl) (mp 163–4°C) (*3*)	25	3.97	2.2723	−0.459	1.14288	315.60	92.5	3.26
		45	3.78	2.2349	−0.467	1.16839	313.97	92.5	3.36
(VI)	Bis(*o*-diacetylaminophenyl) (mp 135–6°C) (*6*)	25	3.87	2.2730	−0.382	1.14227	396.87	108.8	3.71
		45	3.77	2.2353	−0.374	1.16751	404.35	108.8	3.88
(VII)	Bis(5-chloro-2-aminophenyl) (mp 111–2°C (*18*)	25	5.20	2.2712	−0.525	1.14287	368.88	85.6	3.69
		45	4.71	2.2346	−0.574	1.16823	347.13	85.6	3.66

$\alpha = d\epsilon_{12}/dw_2$. $\beta = dv_{12}/dw_2$. $\epsilon_{10} = \lim_{w_2 \to 0} \epsilon_{12}$. $v_{10} = \lim_{w_2 \to 0} v_{12}$.

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Vapor-Liquid Equilibrium of Methane–Propane System at Low Temperatures and High Pressures

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Experimental techniques were developed to sample and analyze vapor-liquid equilibrium phases containing as little as 0.00001 mole fraction propane, which were used for measurements both at near-critical and at considerably dilute conditions. Binary compositions, temperature, pressure, and *K*-values are reported and graphically illustrated for ten isotherms from −75° to −225°F and pressures from 25–950 psia. Error analysis gives an average total relative error in the *K*-values of 1.6%, but for the vast majority of measurements the error is less than 1%.

No vapor-liquid equilibrium data for the methane–propane system in the low temperature range have been reported since the measurements of Price and Kobayashi (*3*). Increased industrial operation at these conditions and improvements in analytical techniques justify investigations at low temperature conditions.

EXPERIMENTAL APPARATUS

The apparatus was the vapor-recycle type reported by Chang et al. (*2*). Significant changes were made in the sampling system. A complete description of the equipment is available (*5*).

A simplified schematic line diagram of the apparatus is given in Figure 1. Cylinders for methane, ethane, and propane are shown. Subsequently the methane–ethane system and the ternary system were investigated, reports of which will appear in this Journal. The gases were charged to the equilibrium cell, made from a Jerguson high-pressure liquid-level gage. The vapor was recirculated through the equilibrium cell. Phase samples were analyzed by chromatography. The Dewar flask was mounted in a Riki box, so that it could be lowered without moving the equilibrium cell or any flow lines.

Special microregulating sampling valves with a temperature compensated packing gland were mounted directly on the equilibrium cell body with a temperature compensated seal arrangement. These sampling valves were used simultaneously for expansion of the high-pressure sample to atmospheric pressure and for sample flow rate control. The liquid-phase sample line capillary ended in the center of the equilibrium cell at the lowest possible position to ensure that samples were drawn from the condensed phase. The vapor-phase capillary tube protruded from the cell wall into the equilibrium chamber near the top of the cell window. The dead volume for both sampling systems from the orifice of the capillary to the needle of the valve was approximately 0.06 ml.

The procedure for the sampling of phases into the gas chromatograph was changed after preliminary investigations of the liquid phase gave nonreproducible results. The cause was in-

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