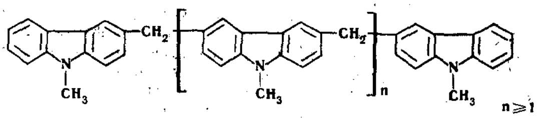
yellow amorphous powder, condensate C. The positions of the bands in the two substances (Fig. 2) is practically the same. However, the high intensity of the bands at 812 and 792 cm^{-1} (appearing when a substituent is put at position 3 in N-methylcarbazole) in comparison with the band at 743 cm^{-1} (1, 2-disubstituted benzene ring in the N-methylcarbazole molecule) in the IR spectrum of condensate C is to be noted. These results, the very low solubility of condensate C in organic solvents, as well as its showing plasticity at about 320° C, are in agreement with the hypothesis that reaction of N-methylcarbazole with formaldehyde under conditions of acid catalysts, gives linear condensation products, e.g.,



EXPERIMENTAL

Condensate A. A solution of 3.34 g (0.02 mole) carbazole and 1.52 ml (0.02 mole) 37% CH_2O in 100 ml acetone, was added dropwise to 300 ml conc HCl, at 20° C, which was kept stirred. After 3 hr the products were poured into 500 ml water, the solid filtered off, dried, and exhaustively extracted with benzene. The product was a pale sulfur-yellow powder, yield 1.65 g (46%, calculated on the fragment $C_{12}H_8NCH_2$), condensate A. IR spectrum: 2925, 2855, 1635, 1607, 1492, 1460, 1380, 1328, 1278, 1234, 1212, 1154, 1026, 924, 880, 800, 745, 722 cm^{-1}. IR spectrum of carbazole: 3410, 1632, 1609, 1497, 1454, 1341, 1242, 1211, 1144, 1013, 931, 914, 857, 749, 723 cm^{-1}.

Condensate B. 1–2 Drops conc H_2SO_4 was added to a gently refluxing solution of 3.34 g (0.02 mole) carbazole and 1.52 ml (0.02 mole) 37% CH_2O in 150 ml glacial AcOH, and heating continued for a further 20 min, the products cooled, and condensate B isolated similarly to condensate A.

Reaction of N-methylcarbazole with formaldehyde. A solution of 10 g (0.055 mole) N-methylcarbazole and 1.71 ml (0.0275 mole) 37% CH_2O in 50 ml acetone was dripped into 150 ml conc HCl, and the mixture stirred for 3 hr at 20° C. The products were then poured into 500 ml water, the precipitate filtered off, washed with water, dried, and the unreacted N-methylcarbazole extracted with MeOH (yield 4 g). The solid was then extracted with benzene, and the extract chromatographed (Al_2O_3, benzene), to give compound I, as white minute crystals, mp 223°–224° (ex benzene). Found: C 86.86; 86.75; H 6.09; 6.15; N 7.50; 7.59%; M 370; 389, calculated for $C_{27}H_{22}N_2$: C 86.8; H 5.74; N 7.48%; M 374. IR spectrum: 2925; 2852, 1635, 1602, 1495, 1427, 1361, 1328, 1250, 1154, 1020, 923, 880, 812 and 792, 767, 743, 723 cm^{-1}. The residue remaining after extraction was condensate C, a pale sulfur-yellow powder, very slightly soluble in organic solvents, softening point 315°–320° C. IR spectrum: the positions of the bands fully duplicate the IR spectrum of compound I.

The IR spectra were determined with an IKS-14 spectrophotometer: a) regions 3600–3100 cm^{-1} and 1800–700 cm^{-1} using vaseline mulls (LiF and NaCl prisms); b) region 2800–3100 cm^{-1} tableted with KBr (LiF prism).

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Mendeleev Moscow Institute of Chemistry and Technology

ELECTRONIC STRUCTURES AND DIPOLE MOMENTS OF 4- AND 5-PHENYL-1, 2-DITHIOL-3-THIONES

M. G. Voronkov, V. I. Minkin, O. A. Osipov, M. G. Kogan, and T. V. Lapina

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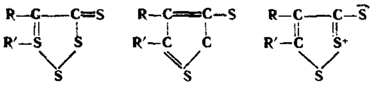
The simple LCAO MO method is used to calculate π-electron configurations of 1, 2-dithiol-3-thione and its 4- and 5-phenyl derivatives. In these compounds the heterocyclic ring has an aromatic character, but the S—S bond is almost excluded from conjugation. The phenyl group in 4-phenyl-1, 2-dithiol-3-thione is an electron acceptor, whereas in the 5 isomer it is an electron donor. The exocyclic sulfur atom has considerable negative charge, while the two endocyclic ones are positively charged. The dipole moments of 4- and 5-phenyl-1, 2-dithiol-3-thione are determined, and the values found are compared with the calculated ones.

In recent years 1, 2-dithiol-3-thione (I) has acquired considerable theoretical and practical interest [1–6].



I II III

X-ray investigation of 4-methyl-1, 2-dithiol-3-thione (Fig. 1) [7] and 1, 2-dithiol-3-thione [8], show the aromatic nature of the ring, the lengths of the C—C and C—S bonds being close to those corresponding bonds in benzene and thiophene [9]. However, the S—S bond in I does not differ in length from the bond between sulfur atoms in the S_8 molecule and saturated

Dipole Moments of 4- and 5-Phenyl-1, 2-dithiol-3-thiones

I	N, mole fractions × $\times 10^5$	α_{mean}	β_{mean}	P_∞, cm³	R	μ, D
$R=H$, $R'=C_6H_5$	327—137	10.33	1.165	385.6	77.8	3.88
$R=C_6H_5$; $R'=H$	231—131	12.56	1.185	459.5	76.3	4.32

disulfides. Hence, it could be inferred [7] that the heterocyclic ring of 1, 2-dithiol-3-thione can be represented as a hybrid of resonance structures I, II, and III in the ratio 5:4:1.

We have computed the π-electron configurations of I and its 4- and 5-phenyl substitution products, by the simple LCAO MO method.

The parameters of [11, 12] were used for the sulfur atoms in the various valence states, but the S—S bond was assigned a value $\beta = 0.3\beta°$, which is in better agreement with the data of Fig. 1. Molecular diagrams IV–VI (Fig. 2) show the results of the computations. For comparison, Fig. 3 shows the molecular diagram of I as obtained using a simplified modification of the self-consistent field method [10].

The low orders of the S—S π bonds found for IV–VI (0.07–0.08) is in good agreement with the length of 2.04 Å for that bond [7], and corresponds to the S—S distance in the S_8, H_2S_2, and Alk_2S_2 molecules (2.04 ± ± Å [9]). The orders of the other bonds in the heterocyclic ring are also in qualitative agreement with the bond lengths (Fig. 1) and aromatic nature of I. However, attempts to correlate lengths and orders of bonds in type I compounds quantitatively, e.g., by linear extrapolation, as in [10], lack adequate foundations.

It is quite interesting that the phenyl group in V is an electron acceptor, and that in VI an electron donor, its character being determined by the charge on the ring carbon atom to which it is attached. Correspondingly, the aromatic ring of molecule V would be expected to enter more easily into reaction with electrophilic reagents, and the aromatic ring of molecule VI more easily into reaction with nucleophilic ones.

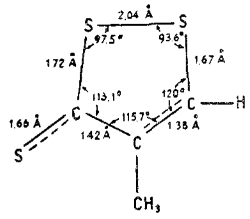


Fig. 1. Structure of the 4-methyl-1, 2-dithiol-3-thione molecule [7].

A considerable negative charge is concentrated on the exocyclic sulfur atom, because of the tendency of the heterocyclic ring to assume a stable aromatic 6-electron configuration due to the expulsion of an odd π electron from the heterocyclic ring.

Compounds of such a type must be characterized by a high polarity, in agreement with the results of measurements of dipole moments of compounds V and VI given in the table.

The dipole moments of compounds V and VI were also calculated, starting from the ascertained distribution of π-electron charges and the precise geometry of the molecule [7]. The values found for the vectors

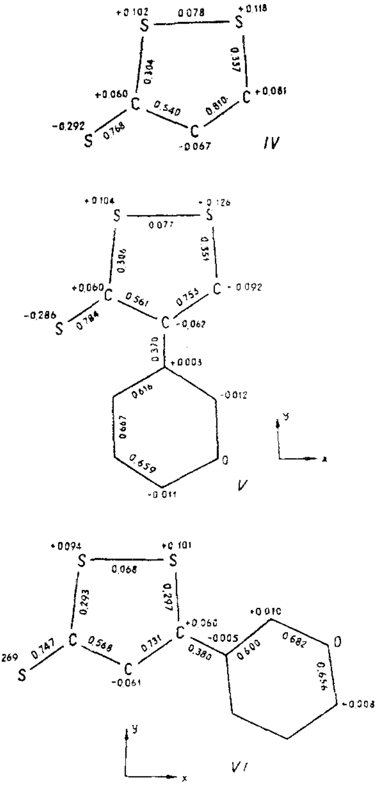


Fig. 2. Molecular diagrams for 1, 2-dithiol-3-one (IV), 4-phenyl-1, 2-dithiol-3-thione (V), and 5-phenyl-1, 2, dithiol-3-thione (VI).

of the σ, π-components and the total dipole moments of V and VI are given below. δ-Moments were calculated as in [13].

V	VI
$\vec{\mu}_\pi = -4.15\vec{i} - 3.33\vec{j}$	$\vec{\mu}_\pi = -3.78\vec{j} - 2.20\vec{j}$
$\vec{\mu}_\sigma = -1.09\vec{i} + 2.07\vec{j}$	$\vec{\mu}_\sigma = -1.09\vec{i} + 2.07\vec{j}$
$\vec{\mu} = -5.24\vec{i} - 1.26\vec{j}$	$\vec{\mu} = \vec{\mu}_\pi + \vec{\mu}_\sigma = -4.87\vec{i} - 0.13\vec{j}$
$\lvert\vec{\mu}\rvert = 5.38D$	$\lvert\vec{\mu}\rvert = 4.88D$

There is rather good agreement between the calculated and experimental values of the dipole moment of VI. For V the agreement between the calculated and experimental values of μ are much worse (discrepancy of 1.5 D). In both cases the experimental values of the dipole moments are lower than the calculated ones, which can be accounted for by the general tendency of the simple MO method, which overestimates charge separation. We note, however, that the dipole moment calculated by us for 1, 2-dithiol-3-thione (Fig. 2) using Bergson's electron configuration [10] is 9.05 D. That value is impermissibly greater than the dipole moment that is expected from the table's data for that compound, which should lie inside the values of the moments of its phenyl derivatives.

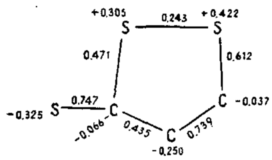


Fig. 3. Molecular diagram of 1, 2-dithiol-3-thione [10].

The dipole moment of 1, 2-dithiol-3-thione, calculated from the electron distribution of IV that we obtained, is 5.25 D. Thus the π-electron configurations of IV–VI correspond better to the actual electron density distribution in type I compounds than to the π-electron configuration shown in Fig. 2. The reason for this is obviously poor choice [10] of starting parameters.

Compounds V [14] and VI [15] were synthesized by methods previously described. The dipole moments were determined as described in [16]. The LCAO MO calculations were made on a EVM M-20 computer using the program of [17].

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Rostov-on-Don State University,
Institute of Organic Synthesis
AS Latvian SSR, Riga

SYNTHESIS AND OPTICAL PROPERTIES OF β-ARYLETHYLENE DERIVATIVES OF 2, 5-DIPHENYLOXAZOLE

V. I. Grigor'eva and B. M. Krasovitskii

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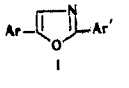
A series of arylethylene derivatives of 2,5-diphenyloxazole derivatives is synthesized, and the absorption and fluorescent spectra of their toluene solutions are investigated. Joining in one molecule of 2, 5-diphenyloxazole and arylethylene groups leads to long wave displacement of the absorption and fluorescence bands, and in most cases to greater intensity of absorption and increase in the photoluminescence quantum yield.

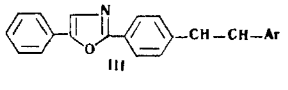
Many 2, 5-diaryloxazoles (I) and diarylethylenes (II) belong to the class of effective organic luminophors [1–3]. It was of interest to unite in one molecule the structural groups of 2, 5-diphenyloxazole and various diarylethylenes, and to investigate the absorption spectra and fluorescent properties of such compounds (III).



I

Ar—CH=CH—Ar′

II



III

Ar and Ar' are identical or different radicals.