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BENZENOID-QUINOID TAUTOMERISM OF AZOMETHINES AND THEIR STRUCTURAL ANALOGUES

XXX *. MOLECULAR STRUCTURE OF GALLIUM AND BORON ORGANOMETALLIC COMPOUNDS WITH TAUTOMERIC AZOMETHINES

V.I. BREGADZE *, N.G. FURMANOVA, L.M. GOLUBINSKAYA, O.Y. KOMPAN, Y.T. STRUCHKOV

Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Vavilov St. 28, Moscow 117813 (U.S.S.R.)

V.A. BREN, Zh.V. BREN *, A.E. LYUBARSKAYA, V.I. MINKIN and L.M. SITKINA

Rostov-on-Don State University, Chemistry Department, Pushinskaya St. 150, Rostov 344006 (U.S.S.R.)

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Summary

The electronic structure and conformations of a systematic series of dimethylgallium and diphenylboron derivatives of aromatic and heterocyclic hydroxy- and mercaptoazomethines have been studied using the methods of electron absorption and emission spectroscopy and dipole moments. Although their phenyl- and methylmercury analogues tend to undergo tautomeric transformations, organometallic compounds of gallium and boron have in solution a mesomeric intra-complex structure with tetracoordinated gallium and boron. The molecular structure of two gallium chelates, dimethylgallium *N*-methylsalicylaldiminate and 2-(*N*-phenylaminomethylene)-3(2H)-benzo(b)furanthionate, have been determined by X-ray diffraction analysis. Structural parameters indicate that chelate formation causes a considerable redistribution of bond lengths in the ligand.

The influence of solvent and structural factors on the position of prototropic (M = H) tautomeric equilibria of the aromatic and the heterocyclic azomethines

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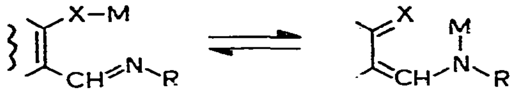
* Communication XXIX see ref. 1.

has been comprehensively studied experimentally and theoretically [2,3].

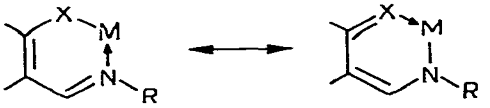


(IA) (IB)

M = H, $HgCH_3$, HgC_6H_5

Annelation of the hydroxy(mercapto)enimine group to a heterocycle or an arene group shifts the equilibrium towards the quinoid tautomer of type B. The same effect is produced by passing from hydroxy (X = O) and mercapto (X = S) to hydroseleno (X = Se) derivatives. The changeover from the above compounds (M = H) to their organometallic derivatives with phenyl- and methylmercury migrants (M = HgR) changes the character of equilibria. According to spectral [4,5] and X-ray diffraction [6] data, such migrants with a "soft" acid moiety are preferably coordinated to the "soft" basic center: nitrogen in hydroxymethines and sulfur in mercaptoazomethines. This results, correspondingly, in forms B and A. Although an additional intramolecular coordination exists in these forms [6], the displacement of M group between X and N donor centers is determined by the double-well potential with structures A and B as the minima. For salicylaldimine derivatives, the difference in their levels is small; thermal and photochromic properties have been investigated for these compounds [4].

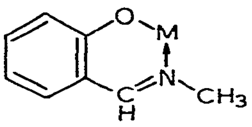
One could expect that, as distinct from organomercury compounds A and B with a quite different degree of covalency of the Hg—X and the Hg—N bond, in the corresponding organometallic compounds of Group III elements, displaying a greater tendency to increase their coordination number, both bonds with the donor center would be more equalized. In this case the displacement of M (GaR_2, Br_2) between X and N donor centers conforms to the intramolecular oscillation described by the single-well potential. Instead of the metallotropic tautomeric equilibrium of structures A and B, the mesomeric structure of type C metal chelate compound will be realized.



(IC)

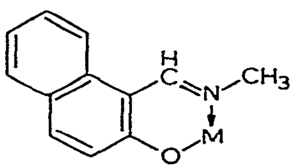
M = GaR_2, BR_2
R = CH_3, F

In order to investigate the molecular structure of compounds that include the above group we studied electron absorption, luminescence and IR spectra



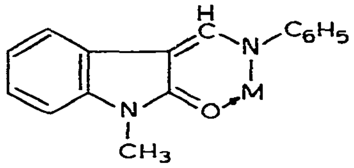
(II)

(1, M = $Ga(CH_3)_2$
7, M = $B(C_6H_5)_2$
8, M = BF_2)



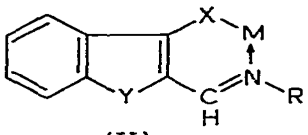
(III)

(2, M = $Ga(CH_3)_2$
9, M = $B(C_6H_5)_2$
10, M = BF_2)



(IV)

(3, M = $Ga(CH_3)_2$
11, M = $B(C_6H_5)_2$)

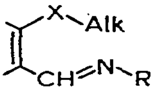

(V)

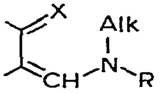
(4, $Y = CO$; $X = O$; $M = Ga(CH_3)_2$; $R = C_6H_5$
5, $Y = O$; $X = S$; $M = Ga(CH_3)_2$; $R = C_6H_5$
6, $Y = S$; $X = S$; $M = Ga(CH_3)_2$; $R = CH_2C_6H_5$
12, $Y = CO$; $X = O$; $M = B(C_6H_5)_2$; $R = C_6H_5$)

and determined the dipole moments for a systematic series of organogallium and organoboron compounds, types II—V. For two organogallium compounds (1 and 5) a full X-ray diffraction study of their molecule in a crystal was performed.

Results and discussion

Electronic spectra are extremely sensitive to the type of the structure (A—C) in prototropic and metallotropic tautomers of hydroxy- and mercapto-azomethine compounds of both the aromatic [7,8] and the heterocyclic [9,10] series. Compounds possessing fragments VIA and VIB can serve as models structures Ia and IB.


(VI A)


(VI B)

Form B has a characteristic long-wave absorption band, whereas the spectrum of type A compounds is shifted into the short-wave region. Compounds V (Y = CO, X = O) are an exception: their hydroxyvinylimine structure, A, absorbs at 100 nm in a longer wave-length region of the spectrum than B [11].

Molecules of II—V with type C tetracoordination are modeled by diphenyl- or difluoro-boron derivatives of II—V ($M = BPh_2$ and BF_2) [12]. We synthesized such compounds (7—12) by interaction of the corresponding ligands of I—IV (M = H) with diphenylboronic acid anhydride or with its 2-aminoethyl ether using procedures similar to those described earlier [13,14]. Spectral characteristics of the compounds studied are given in Table 1 and Figs. 1 and 2.

The dimethylgallium derivatives (1—6) do not display any solvato- and thermo-chromism characteristic of dynamic tautomeric systems. This means that either the IA $\rightleftharpoons$ IB equilibrium is shifted well towards one of these forms or these compounds have a mesomeric structure of the IC type.

The absorption spectra of the *N*-methylsalicylaldimine dimethylgallium derivative (1) in different solvents (Fig. 1) differ considerably from the spectrum in hexane of the corresponding ligand, which in a non-polar solvent has a benzoid structure of the IA type. At the same time, the two intensive absorption bands observed conform to a hypsochromically shifted spectrum calculated [8] for a quinoid tautomer of the IB type (M = H). The absorption spec-

TABLE 1

ELECTRONIC AND INFRARED SPECTRA OF COMPOUNDS II—V

Comp.	Type	M	UV-spectra		IR-spectra ν, (cm^{-1}) (Nujol mull)	Luminescence Spectra λ_{max}(nm) (T = 293° C)
			Solvent	λ_{max}(nm) ($\epsilon \times 10^{-3}$)		
1	II	$Ga(CH_3)_2$	H	282 (7.0) 387 (4.4)		
			CH_3CN	280 (5.8) 372 (4.0)	1595, 1640	440
2	III	$Ga(CH_3)_2$	H	313 (7.6) 325 (8.8) 400 (6.4) 412 (6.1)	1520, 1630	460
			CH_3CN	317 (5.8) 323 (6.7) 393 (5.5) 405 (5.6)		
3	IV	$Ga(CH_3)_2$	H	285 (15.4) 373 (20.7) 386 (23.2)		
			CH_3CN	285 (14.2) 372 (20.8) 384 (22.2)	1520, 1555, 1630	460
			DMSO	285 (10.4 375 (18.3) 382 (18.3)		
4	V Y = CO	$Ga(CH_3)_2$	H	304 (7.7) 368 (24.6) 460 (9.5)	1515, 1585, 1625, 1650, 1685	560
	X = O		CH_3CN	301 (5.1) 368 (26.4) 445 (9.4)		
	R = C_6H_5		DMSO	305 (5.6) 372 (27.6) 442 (10.0)		
5	V	$Ga(CH_3)_2$	H	310 (8.6) 348 (15.7) 470 (11.0)		
	Y = O		CH_3CN	305 (8.8) 346 (12.7) 445 (9.8) 510 (4.9)	1520, 1565, 1590, 1610	540 [a]
	X = S		DMSO	310 (13.1) 350 (8.2) 510 (2.0)		
	R = C_6H_5					
6	V	$Ga(CH_3)_2$	H	282 (12.0) 340 (10.3) 450 (4.0) 500 (3.1)		
	Y = S		CH_3CN	275 (9.4) 337 (8.5) 428 (3.3) 485 (3.0)	1585, 1605	500 [a]
	Y = S		DMSO	290 (10.6) 342 (12.3) 470 (4.9) 495 (5.2)		
	R = $CH_2C_6H_5$					
7	II	BPh_2	B	285 (8.7) 385 (3.5)	1565, 1615, 1650	490
			DMSO	283 (9.0) 375 (3.4)		
8	II	BF_2	DCE	271 (15.4) 348 (4.4)	1575, 1620, 1668	—
9	III	BPh_2	B	335 (8.4) 397 (4.8)	1525, 1560, 1595, 1640	500
			DMSO	328 (8.4) 397 (4.8)		
10	III	BF_2	DCE	248 (13.6) 330 (8.4) 370 (6.9) 385 (5.9)	1530, 1570, 1625, 1650	—
11	IV	BPh_2	B	284 (16.5) 380 (27.0)	1520, 1605, 1640	500
12	V	BPh_2	B	315 (164.) 355 (15.2) 440 (5.2)		
	Y = CO	Y = CO	CH_3CN	310 (17.4) 350 (16.7) 440 (5.0)	1525, 1590, 1625, 1710	—
	X = O		DMSO	312 (16.2) 353 (15.5) 440 (4.7)		
	R = C_6H_5					

H = hexane, DMSO = dimethylsulfoxide, DCE = dichloroethane, B = benzene [a] T = 77°K

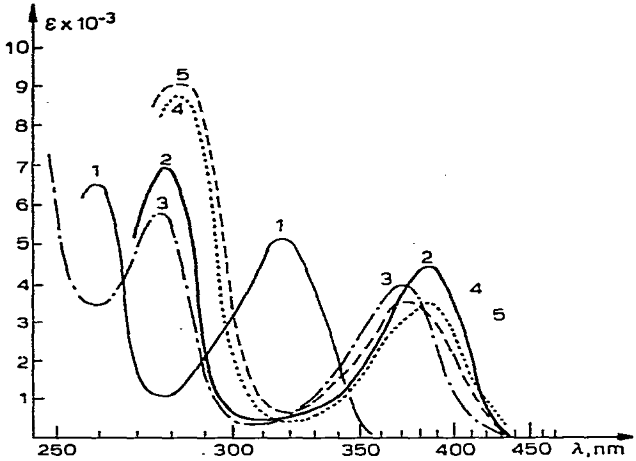


Fig. 1. Electron absorption spectra. (1) salicylalmethylimine in hexane, (2, 3) its dimethylgallium derivative (1) in benzene and acetonitrile, respectively, (4, 5) its diphenylboron derivative (7) in benzene and dimethylsulfoxide, respectively.

tra of the diphenylboron analogue (7) are quite similar to the spectrum of compound 1.

Analogous spectral properties are displayed by the 2-phenylaminomethylenefuran-3-thione dimethylgallium derivative (Fig. 2). The two long-wave bands in the visible portion of the spectrum are hypsochromically shifted as compared with the spectrum of fixed quinoid form IVB (X = S) and differ markedly from the *S*-alkyl structure VIA (X = S) [9].

All the dimethylgallium compounds (1—6) display intensive luminescence, with a number of them (1—4) luminescing at room temperature (Table 1). The

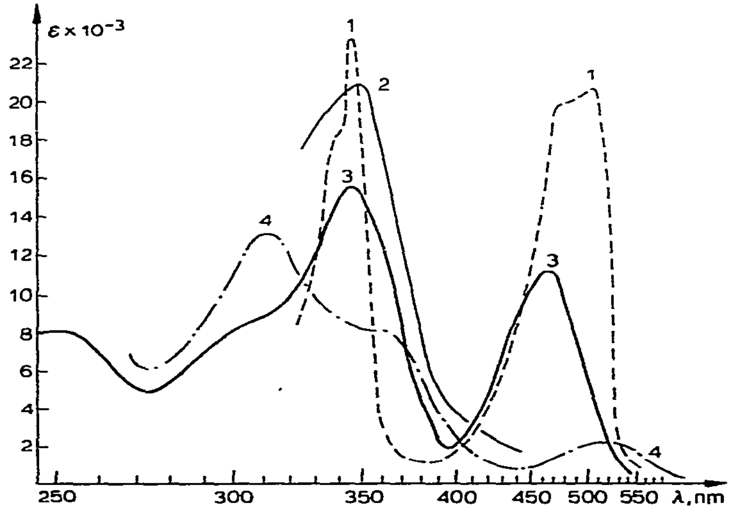


Fig. 2. Electron absorption spectra. (1, 3) benzofuranthion-2-morpholinomethide in acetone, (2) 3-methylmercaptobenzofuran-2-aldanile in acetone, (3,4)2-(*N*-phenylaminomethylene)-3(2H)-benzo(b) furanthionate of dimethyl gallium (5) in hexane and dimethylsulfoxide, respectively.

TABLE 2

DIPOLE MOMENTS OF ORGANO-GALLIUM AND -BORON DERIVATIVES OF HYDROXY- AND MERCAPTO-AZOMETHINES, (BENZENE, 30°C).

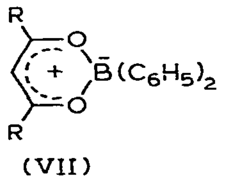
Compound			Concentration (mol. fraction)	P_∞(cm^3)	P_e (cm^3)	μ(D)
	type	M				
1	II	$Ga(CH_3)_2$	0.0009—0.0043	375.9	57.8	3.98
2	III	$Ga(CH_3)_2$	0.0010—0.0033	311.2	73.7	3.44
3	IV	$Ga(CH_3)_2$	0.0011—0.0035	154.3	92.4	1.76
5	V	$Ga(CH_3)_2$	0.0008—0.0039	330.6	93.0	3.44
6	V	$Ga(CH_3)_2$	0.0010—0.0025	372.4	103.2	3.67
7	II	BPh_2	0.0014—0.0030	581.3	91.2	4.94
8	II	BF_2	0.0010	777.0	58.5	6.00
9	III	BPh_2	0.0008—0.0016	584.5	107.0	4.88
10	III	BF_2	0.0010—0.0023	775.9	43.2	6.05
11	IV	BPh_2	0.0008	416.8	125.7	3.81

ligands do not have such properties. In compounds 5 and 6 luminescence with a maximum of 500—540 nm is caused by the excitation of their molecules in the 400—460 nm band corresponding to long-wave absorption. The fluorescence spectra of diphenylboron derivatives (7, 9, 11) are similar but have a somewhat greater Stokes shift.

Based on the data from absorption spectra it can thus be assumed that dimethylgallium and diphenylboron derivatives of hydroxy- and mercaptoazomethines either have a structure of the IB type or exist in the tetracoordinated IC form. The latter assumption is supported by considerable differences in the emission spectra from the ligands.

The type IC chelate tetracoordinated structure requiring some transfer of charge onto the metal atom is also in agreement with the rather high dipole moment values of organogallium and organoboron derivatives (Table 2).

Dipole moments of diphenylborazomethines amount to 4—5 D (Table 2). For comparison we can take the values of dipole moments for diphenylboron chelates, type VII [15].



(VII)

$R = CH_3$ $\mu = 4.90$ D

$R = C_6H_5$ $\mu = 5.59$ D

The replacement of a diphenylboron group by a more polar BF_2 group (compounds 8 and 10) raises the dipole moment to 6 D. The change-over from diphenylboron to dimethylgallium chelates decreases the polarity of the structure and, correspondingly, the values of dipole moments by 1—1.5 D (Table 2).

A chelated structure with tetracoordinated central boron and gallium atoms explains the considerable low-frequency shift (15—50 cm^{-1}) of the vibrational bands of carbonyl groups (Table 1) as compared with the spectra of initial ligands [5,9—11].

The nature of the bonding in the boron and gallium complexes (II—V) is nearly identical but the coordination of diphenylboron moiety in the chelate node is more rigid. This is indicated by the following facts.

(i) For diphenyl- or difluoro-boron complexes (II—V) to be synthesized the presence of a hard nucleophilic center (e.g., an oxygen atom) in the ligand is necessary. All our attempts to obtain diphenylboron derivatives (Y, X = S) of azomethines containing soft donor atoms, nitrogen and sulfur, ended in failure. Gallium complexes are, however, formed in this case.

(ii) Boron chelates are more stable to hydrolysis than similar gallium compounds.

(iii) In polar and basic solvents of the dimethylsulfoxide, pyridine or triethylamine types the electronic absorption spectra of diphenylboron derivatives do not undergo any substantial changes, whereas the spectra of dimethylgallium compounds are sensitive to the type of solvent, which is probably associated with changes in the character of internal coordination. This is especially clearly seen in compounds 5 and 6 with the R_2GaNS mode (Table 1, Fig. 2). An unambiguous proof of gallium tetracoordination in chelate dimethylgallium derivatives of hydroxy- and mercapto-azomethines in the solid phase has been contained from the X-ray diffraction study of compounds II ($M = Ga(CH_3)_2$) and V ($M = Ga(CH_3)_2$, $Y = O$, $X = S$) (1, 5).

The structure of dimethylgallium *N*-methylsalicylaldiminate (1) and its interatomic distances are shown in Fig. 3, the valence angles are given in Table 3.

As distinct from dimethylgallium salicylaldehydate with its dimeric structure VIII [16], the molecule of compound 1 is monomeric, and the gallium atom has tetrahedral coordination distorted by the closure of the six-membered heterocycle: the N—Ga—O angle in the cycle is 91.3(3)°, and the exocyclic C(9)—Ga—C(10) angle is increased to 126.2(6)°. The heterocycle is not planar:

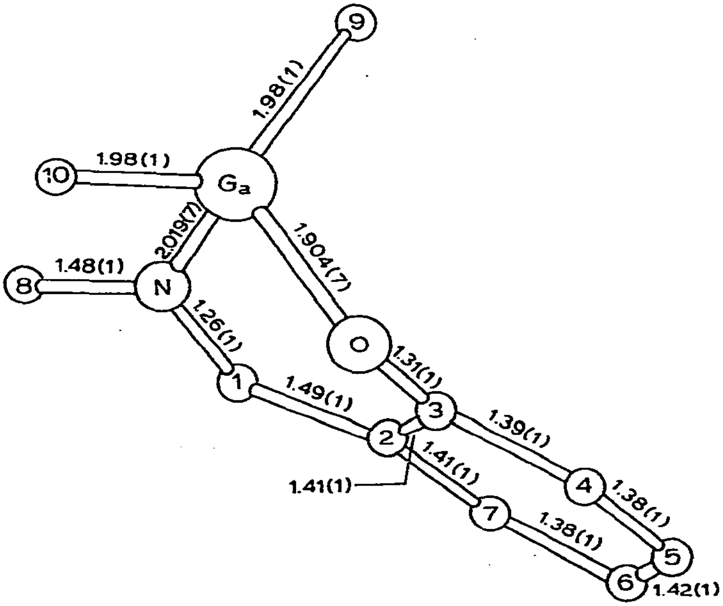


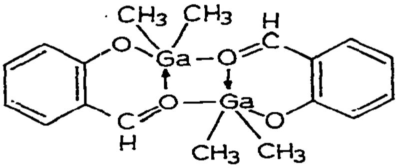
Fig. 3. Molecule of dimethylgallium *N*-methylsalicylaldiminate (compound 1).

TABLE 3

VALENCE ANGLES IN THE MOLECULE OF DIMETHYLGALLIUM *N*-METHYLSALICYLALDIMINATE II ($M = Ga(CH_3)_2$)

Angle	ω(°)	Angle	ω(°)
OGaN	91.9(3)	C(1)C(2)C(3)	123.2(8)
OGaC(9)	110.9(5)	C(1)C(2)C(7)	115.1(7)
OGaC(10)	108.0(5)	C(3)C(2)C(7)	121.7(9)
NGaC(10)	110.9(4)	OC(3)C(2)	123.7(9)
NGaC(9)	103.5(5)	OC(3)C(4)	119.1(8)
C(9)GaC(10)	126.2(6)	C(2)C(3)C(4)	117.3(8)
GaOC(3)	123.0(6)	C(3)C(4)C(5)	121.7(10)
GaNC(I)	123.1(7)	C(4)C(5)C(6)	120.4(7)
GaNC(8)	118.8(6)	C(5)C(6)C(7)	118.8(10)
C(8)NC(1)	117.8(8)	C(6)C(7)C(2)	120.1(9)
NC(1)C(2)	12.8(8)		

the O and C(1) atoms are located on the benzene ring plane, and the Ga and N atoms are located 0.82 and 0.24 Å, respectively, away from that plane on the same side of it.



(VIII)

These disturbances of planarity are appreciably greater than in a similar *N,N*-ethylenebis(salicylideniminato)bis(dimethylgallium) molecule where this ring is almost flat [17].

In acetone solution it was impossible to trace the acoplanarity of the molecule (compound 1) and to observe a diastereotopicity of methyl groups with the help of dynamic ^1H and ^{13}C NMR because of the low cycle conversion barrier.

Both Ga—C bonds are of equal length, 1.98(1) Å, characteristic of tetrahedrally coordinated gallium (1.92—1.98 Å) [16—24].

There being no information in the literature on the normal covalent radius of gallium *, the above distances can be used to estimate this radius as approximately 1.21 Å (1.98—0.77 Å). According to this estimation of the radius, the length of the Ga—O covalent bond must be equal to 1.87 Å, and that of the Ga—N bond 1.91 Å. In molecule I the length of the Ba—O bond, 1.904(7) Å, is close to the above value. This bond is slightly shorter than the one in dimethylgallium hydroxide (1.92—1.99 Å) [18], where it is a part of the eight-membered ring, but is longer than in $(GaH)_6(GaH_2)_2(\mu_3\text{-}O)_2(\mu_3\text{-}NCH_2CH_2NMe_2)_4$-

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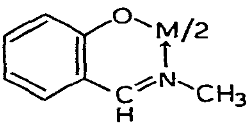
* The universal atomic radius of 1.30 Å cited by Slater [34] cannot be accepted because it was obtained from the data on many different structures and is too "universal". The tetrahedral covalent radius of 1.26 Å cited by Pauling [35] was obtained for the Ga type A structures and also seems to be not quite satisfactory for organic compounds.

$(\mu\text{-NHCH}_2\text{CH}_2\text{NMe}_2)_2$ (1.866—1.876 Å) [24], where it is a part of the four- and six-membered cycles.

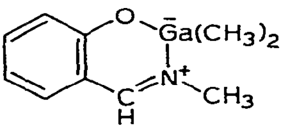
The length of the Ga—N bond in the molecule of compound I, 2.019(7) Å, is 0.1 Å longer than the one calculated using the above estimation of Ga radius and is close to the upper limit of the known experimental values for aromatic and heterocyclic derivatives containing tetrahedral gallium, 1.92—1.98 Å, [16,21—24], with the bond lengths of 2.002 and 2.006 Å in $(Me_2GaN_2C_3H_3)_2$ [21] and 2.033 Å in $(GaNOC_8H_{13})_2$ being regarded as strongly enlarged.

The Ga—N interatomic distance in the molecule (1) is, thus, enlarged and can be regarded as confirming to additional interaction of the M···N type in benzenoid structure IA. Bond lengths in the ligand also indicate the predominance of the benzenoid form in the IC mesomeric hybrid: the bonds in the benzene ring, 1.38(1)—1.41(1) Å, are equalized; the C(1)—N distance, 1.26 Å, is typical of a double C=N bond [25]; and the C(1)—C(2) distance, 1.49 Å, of a single $C(sp^2)$—$C(sp^2)$ bond [26]. A similar distribution of bond lengths in the chelate mode and the ligand is characteristic of chelate compounds of transition metals with *N*-methylsalicylaldimine, IX [27].

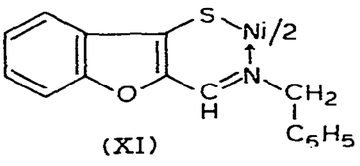
A certain contribution of the quinonoid form is indicated, apart from a strong intramolecular Ga—N interaction, by the shortening the O—C(3) bond to 1.31(1) Å, as compared with 1.38 Å in phenols (see, e.g., [28]). The contribution of quinonoid form to the IC mesomeric structure, however, seems to be small. On the whole, bond length distribution in the molecule is best described by the zwitter-ion formula, X.



(IX, M = Cu, Ni, Pd)



(X)



(XI)

The structure of dimethylgallium 2-(*N*-phenylaminomethylene)-3(2H)-benzo(b)furanthionate (5) and the interatomic distances are shown in Fig. 4. The valence angles are given in Table 4. The Ga atom is included in a six-membered cycle and has a highly distorted tetrahedral configuration: the intracyclic S—Ga—N angle is reduced to 98.0(2)° and the exocyclic C(16)—Ga—C(17) angle enlarged to 123.4(3)°. As in the structure of compound 1, the molecule of 5 is monomeric with both molecules having similar conformations. The C(1)—C(9), O, S portion of the molecule is almost flat. The distance between these atoms and the mid-plane does not exceed 0.046 Å. The angle between this plane and the C(10)···C(15) phenyl ring is 49.2°. The six membered metal-chelate cycle is not planar: the distance from the Ga and N atoms to the C(1)···C(9), O, S plane is 1.00 and 0.86 Å, respectively, i.e., greater than in the dimethylgallium *N*-methylsalicylaldiminate molecule (1).

The Ga—N bond length, 2.055(5) Å, as in the molecule of compound 1, is enlarged in comparison with the length of the usual single bond. There are no data in literature on the length of Ga—S bonds in organic derivatives, but, if we resort to the above mentioned estimation of Ga covalent radius, the length of a Ga—S bond must be equal to 2.25 Å, which means that this bond in molecule 5, 2.321(2) Å, is also somewhat elongated. This indicates that the struc-

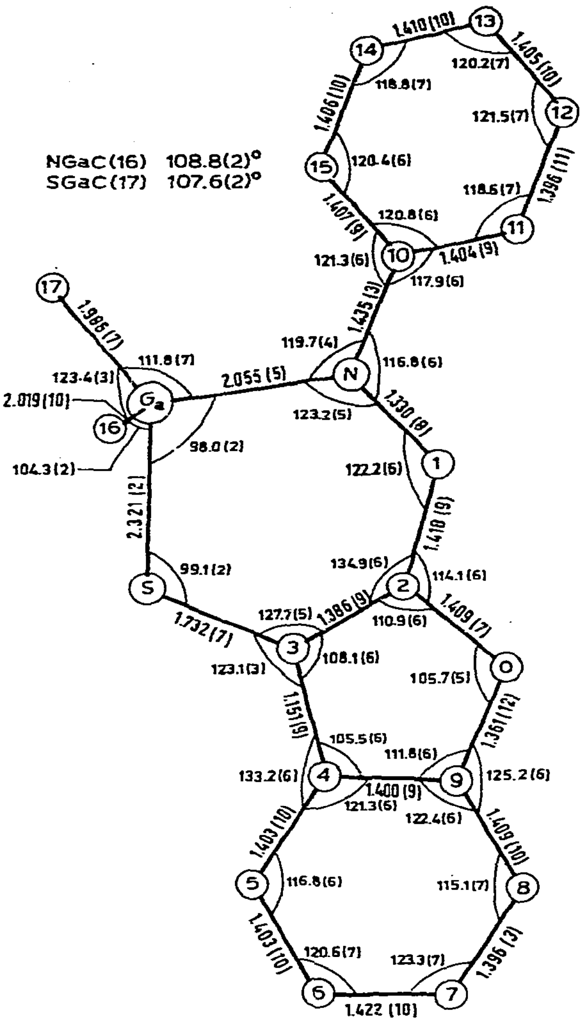


Fig. 4. Molecule of dimethylgallium 2-(*N*-phenylaminomethylene)-3(2H)-benzo(b)furanthionate (compound 5).

ture of molecule 5 is close to the IC type. This is also supported by the distribution of the other bond lengths in the heterocycle and the chelate ring. The bond lengths of C(1)—N, 1.330(8), C(1)—C(2), 1.418(9), and C(2)—C(3), 1.380(9) Å, are close to those usual for aromatic heterocycles [26]. The S—C(3) bond with its length of 1.732(7) Å is also intermediate between the single, 1.817 Å, [26] and the double, 1.62—1.64 Å [29] bond. In the molecule of nickel bis-2-(*N*-benzylaminomethylene)-3(2H)-benzo(b)furanthionate (XI) the lengths of S—C(3), 1.707, and N—C(1), 1.326 Å, bonds are quite close to those of the corresponding bonds in the molecule of the dimethylgallium analogue (5), but the C(1)—C(2) bond length, 1.478 Å, is much greater [30].

TABLE 4

VALENCE ANGLES IN MOLECULE 5

Angle	ω(°)	Angle	ω(°)
NGaS	98.0(2)	C(2)OC(9)	105.7(5)
NGaC(16)	108.8(2)	C(4)C(9)O	111.8(6)
SGaC(17)	107.6(2)	OC(9)C(8)	125.2(6)
SGaC(16)	104.3(2)	C(5)C(4)C(9)	121.3(6)
NGaC(17)	111.8(7)	C(4)C(5)C(6)	116.8(6)
C(16)GaC(17)	123.4(3)	C(5)C(6)C(7)	120.6(7)
GaNC(1)	123.2(5)	C(6)C(7)C(8)	123.3(7)
NC(1)C(2)	122.2(6)	C(7)C(8)C(9)	115.1(7)
C(1)C(2)C(3)	134.9(6)	C(4)C(9)C(8)	122.9(6)
C(2)C(3)S	127.7(5)	GaNC(10)	119.7(4)
GaSC(3)	99.1(2)	C(1)NC(10)	116.8(6)
C(1)C(2)O	114.1(6)	NC(10)C(11)	117.9(6)
OC(2)C(3)	110.9(6)	NC(10)C(15)	121.3(6)
C(2)C(3)C(4)	106.1(6)	C(10C(11)C(12)	118.6(7)
SC(3)C(4)	126.1(5)	C(11)C(12)C(13)	121.3(7)
C(3)C(4)C(5)	133.2(6)	C(12)C(13)C(14)	120.2(7)
C(3)C(4)C(9)	105.5(6)	C(13)C(14)C(15)	118.8(7)
		C(10)C(15)C(14)	120.4(6)

Experimental

Dimethylgallium derivatives of hydroxy- and mercaptoazomethines were synthesized according to earlier described procedures [31].

Diphenylboron derivatives

See Table 5.

Compounds 7, 9. Equimolar quantities of methylsalicyl- or methyl-2-hydroxy-1-naphthaldimines and ethanolamine diphenylborate in methanol or benzene solution were refluxed in a water bath for half an hour. The substances

TABLE 5

THE DIPHENYL- AND DIFLUORINE-BORON DERIVATIVES II—V OF AZOMETHINES

Compounds	mp (°)	Found (calcd.)(%)			Formula
		C	H	B	
7	179—180	79.5 (80.2)	6.2 (6.1)	3.7 (3.6)	$C_{20}H_{18}BNO$
8	125—126	21.2[a] (20.8)	7.7[b] (7.7)		$C_8H_8BF_2NO$
9	190	83.1 (82.6)	5.9 (5.8)	2.7 (3.1)	$C_{24}H_{20}BNO$
10	189—190	16.6[a] (16.3)	6.6[b] (6.0)		$C_{12}H_{10}BF_2NO$
11	185	81.0 (81.2)	5.4 (5.6)	2.9 (2.6)	$C_{28}H_{23}BN_2O$
12	139—140	81.0 (81.3)	5.3 (4.9)	2.4 (2.6)	$C_{28}H_{20}BNO_2$

[a] fluorine, [b] nitrogen

that precipitated after cooling were purified by recrystallization from carbon tetrachloride. The yield is 50—80%.

Compound 11 and 12. Equimolar quantities of 2-phenylaminomethylene derivatives of 1-methyloxindole or 1,3-indandion and borodiphenyl acid anhydride were refluxed in chlorobenzene or dioxan solution, which was followed by removal of the solvent in vacuum. The residue was separated on a chromatographic column (aluminum oxide; benzene-hexane 1: 2), and the first fraction was collected. The yield was 40—50%.

In an attempt to obtain diphenylborates of arylsalicyl- or aryl-2-oxy-1-naphthaldimines by having the ligands react with ethanolamine diphenylborate we could isolate, as opposed to alkylamine diphenylboron derivatives, only the addition products II · $H_2NCH_2CH_2OH$ [M = $B(C_6H_5)_2$] (13) and III · $H_2NCH_2CH_2OH$ [M = $B(C_6H_5)_2$] (14). Bands of frequencies 3400—3500 cm^{-1} (ν(OH), $\nu(NH_2)$) are present in the IR spectra. The PMR spectra of these adducts contain signals at δ 1.82 ppm (13), and 1.60 ppm (14), disappearing on deuteration, and doublets with chemical shifts of 3.40 and 3.08 (13), 3.55 and 3.20 ppm (14) corresponding to methylene groups.

Compound 13; yellow-green crystals. M.p. 145—146° C. Found: C, 75.9; H, 6.2; B, 2.6. $C_{27}H_{27}BN_2O_2$ Calcd.: C, 76.3; H, 6.4; B, 2.6%. IR, $\nu(cm^{-1})$: 1520, 1560, 1615, 1630, 3520.

Compound 14: yellow crystals, m.p. 206°C. Found: C, 78.7; H, 6.0; B, 2.1. $C_{31}H_{29}BN_2O_2$ Calcd.: C, 78.8; H, 6.2; B, 2.3%. IR, $\nu(cm^{-1})$: 1570, 1610, 1645, 3450.

Difluoroborides (8, 10). Compounds 8 and 10 were obtained by refluxing the corresponding ligands with boron trifluoride etherate in chlorobenzene during 3—5 hours [14] (Table 5).

Absorption spectra in the UV and the visible region were recorded on a Specord UV-Vis spectrometer (GDR), IR spectra were obtained on a UR-20 spectrometer and PMR spectra on a Tesla BS-487c spectrometer (80 MHz) at 25° C. Concentration of substances was 10—15% in carbon tetrachloride and methylene chloride. The internal standard was HMDS.

Luminescence spectra were recorded on a Fotolyum installation (TsKB AMN USSR). Solvents: hexane, hexane-isopentane mixture, concentration 10^{-4} *M*.

Dipole moments were measured in benzene at 30°C. The permittivity of solutions was measured by the heterodyne method (concentration of substances 0.001—0.005 mole parts). Electron polarization was taken equal to molecular refraction and calculated from the sum of atomic refractions. The values of polarization at infinite dilution were calculated from Gedestrand's formula [32].

X-ray diffraction studies. The crystals of dimethylgallium salicylaldiminate (compound 1) are monoclinic: a 14.7898(1), b 6.3746(2), c 12.0686(9) Å, β 99.430(8)°, V = 1122.4(3) Å^3, d_{calc} 1.39 g/cm^3, Z = 4, space group $P2_1/c$. Intensities of 1063 independent reflections with $F^2 > 3\sigma$ were measured on a Hilger-Watts four-circle automatic diffractometer controlled by RDR-8/1 minicomputer (λ Cu-K_α, graphite monochromator, $\theta/2\theta$ scanning, $2\theta < 114°$).

The structure was interpreted by direct method in automatic mode with the help of Rentgen-75 programs [33]. In the best E synthesis 8 nonhydrogen atoms were localized. In subsequent electron density synthesis all the nonhy-

TABLE 6

COORDINATES OF ATOMS ($\times 10^4$) IN MOLECULE I

Atom	X	Y	Z
Ga	1714(1)	2211(2)	1345(1)
O	2759(5)	3816(11)	1138(5)
N	2327(5)	1230(12)	2876(6)
C(1)	2965(6)	2225(15)	3468(7)
C(2)	3385(6)	4175(15)	3089(7)
C(3)	3271(6)	4314(16)	1956(8)
C(4)	3730(7)	6624(17)	1713(8)
C(5)	4273(7)	7759(20)	2545(9)
C(6)	4378(7)	7101(19)	3687(9)
C(7)	3943(7)	5302(17)	3943(8)
C(8)	1958(8)	−635(18)	3374(9)
C(9)	718(9)	4055(23)	1682(13)
C(10)	1585(10)	−133(22)	249(10)

drogen atoms were revealed. The structure was refined by the least-squares method, first isotropically to $R = 0.097$ and then anisotropically to $R = 0.074$. Coordinates of atoms and anisotropic temperature parameters are shown in Tables 6 and 7.

The crystals of dimethylgallium 2-(*N*-phenylaminoethylene)benzo(b)-furan-3(2H)-thionate (compound 5) are monoclinic: a 10.223(3), b 7.435(2), c 20.473(5) Å, β 91.13(2)°, $V = 1555.8(7)$ Å^3, d_{calc} 1.51 g/cm^3, $Z = 4$, space group $P2_1/c$. Intensities of 2473 independent reflections with $F^2 > 2\sigma$ and reduced cell parameters were measured at the temperature of −120° C on a Syntex P2$_1$ four-circle automatic diffractometer controlled by Nova-1200 minicomputer (λ Mo-K$_\alpha$, graphite monochromator, $\theta/2\theta$ scanning, $2\theta < 52°$).

The structure was interpreted by heavy atom method and refined in isotropic approximation by least-squares method to $R = 0.065$ and then in anisotropic approximation to $R = 0.056$. All the investigations were carried out in accordance with EXTL programs on Eclipse S/200 computer. Coordinate of atoms and anisotropic temperature parameters are shown in Tables 8 and 9.

TABLE 7

ANISOTROPIC TEMPERATURE PARAMETERS B_{ij} FOR STRUCTURE IN THE EQUATION $T = \exp[-10^{-4}(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ga	51	253	51	−17	16	−11
O	60	342	28	−93	22	40
N	48	163	46	−31	34	8
C(1)	38	146	58	16	41	32
C(2)	30	197	36	32	16	15
C(3)	36	195	50	17	33	43
C(4)	40	269	73	−32	42	24
C(5)	42	300	94	18	38	45
C(6)	45	261	96	36	29	−40
C(7)	51	216	63	−11	27	−25
C(8)	73	211	82	−86	−58	47
C(9)	52	362	177	86	37	28
C(10)	98	354	65	−56	18	−122

TABLE 8

COORDINATES OF ATOMS ($\times 10^4$) IN MOLECULE 5

Atom	X	Y	Z
Ga	2564(1)	2476(1)	1922(1)
S	1210(2)	1037(3)	1164(1)
O	−1941(4)	3255(7)	1945(2)
N	1271(5)	2596(9)	2677(2)
C(1)	−9(7)	2828(8)	2587(3)
C(2)	−626(6)	2689(10)	1963(3)
C(3)	−264(6)	2022(9)	1363(3)
C(4)	−1399(6)	2224(10)	933(3)
C(5)	−1623(7)	1879(10)	261(4)
C(6)	−2865(7)	2313(11)	5(4)
C(7)	−3834(7)	3075(10)	410(4)
C(8)	−3627(7)	3427(10)	1072(4)
C(9)	−2374(7)	2974(9)	1320(3)
C(10)	1758(6)	2616(11)	3339(3)
C(11)	3016(7)	3315(10)	3459(4)
C(12)	3505(7)	3338(11)	4100(4)
C(13)	2770(6)	2662(12)	4618(3)
C(14)	1517(7)	1929(10)	4496(4)
C(15)	1021(7)	1899(10)	3851(3)
C(16)	2792(6)	5053(8)	1647(3)
C(17)	4053(6)	839(11)	2124(4)

TABLE 9

ANISOTROPIC TEMPERATURE PARAMETERS B_{ij} IN STRUCTURE 5 IN FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2o^{*2} + B_{12}hka^*o^* + B_{13}hla^*c + B_{23}kla^*c^*)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	1.03(3)	1.48(3)	1.43(3)	0.16(3)	0.11(2)	0.08(4)
S	1.31(7)	1.69(8)	1.45(7)	0.14(6)	0.19(5)	−0.32(7)
O	1.3(2)	1.2(2)	1.9(2)	0.2(2)	−0.0(2)	0.2(2)
N	1.3(2)	1.0(2)	1.4(2)	0.1(2)	0.1(2)	−0.2(3)
C(I)	1.7(3)	0.3(3)	1.9(3)	−0.3(2)	−0.1(2)	0.3(2)
C(2)	1.2(2)	0.8(3)	1.8(3)	0.2(3)	0.1(2)	0.1(3)
C(3)	1.4(3)	0.9(3)	1.4(3)	−0.3(2)	−0.1(2)	0.2(2)
C(4)	1.4(2)	0.8(3)	2.1(3)	−0.3(2)	0.0(2)	0.4(3)
C(5)	2.3(3)	1.1(3)	2.0(3)	−0.8(2)	−0.7(3)	0.3(3)
C(6)	2.3(3)	1.2(3)	2.3(3)	−0.4(3)	−0.4(3)	0.5(3)
C(7)	2.2(3)	1.3(3)	2.8(4)	−0.6(3)	−0.6(3)	−0.6(3)
C(8)	1.9(3)	1.1(3)	2.5(4)	−0.4(3)	−0.7(3)	0.5(3)
C(9)	1.8(3)	0.7(3)	1.9(3)	−0.2(2)	−0.2(2)	0.1(2)
C(10)	1.7(3)	0.7(3)	1.6(3)	0.6(3)	0.02(2)	-0.1(3)
C(11)	1.5(3)	1.2(3)	2.3(3)	0.5(2)	−0.4(3)	−0.5(3)
C(12)	2.0(3)	1.5(3)	2.3(4)	0.8(3)	−0.1(3)	−0.6(3)
C(13)	1.8(3)	1.6(3)	1.9(3)	0.9(3)	−0.2(2)	−0.4(3)
C(14)	1.9(3)	1.3(3)	2.1(3)	0.8(2)	−0.1(3)	−0.3(3)
C(15)	1.9(3)	1.0(3)	1.4(3)	0.6(2)	0.3(2)	−0.1(2)
C(16)	0.9(2)	0.3(3)	2.0(3)	−0.3(2)	0.3(2)	0.7(2)
C(17)	1.9(3)	1.9(4)	2.9(4)	0.6(3)	0.1(3)	0.4(3)

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