Synthesis of 1,3-bis(acetylacetonyloxy)- and 1,3-bis(benzoylacetonyloxy)benzene and their complexation with lanthanide ions

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Claisen condensation of 1,3-bis(methoxycarbonylmethoxy)benzene with acetone and acetophenone afforded new chelating ligands consisting of two β-diketonate fragments, *viz.*, 1,3-bis(acetylacetonyloxy)benzene and 1,3-bis(benzoylacetonyloxy)benzene, which are linked to each other through the resorcinol spacer. In the crystal, 1,3-bis(acetylacetonyloxy)benzene, unlike the starting ester, adopts a planar conformation and exists in the enol form. The acidities of these compounds and their complexation with lanthanide ions in aqueous-ethanolic solutions were studied by pH-potentiometry. Depending on the concentration conditions and pH, the La^{3+}, Gd^{3+}, and Lu^{3+} ions form 1 : 1, 1 : 2, or 1 : 3 complexes with bis(β-diketones). The stability of the complexes increases as the atomic number of the lanthanide increases ($La^{3+} < Gd^{3+} \leq Lu^{3+}$). The complexation constants and selectivity of complexation substantially increase with increasing degree of deprotonation of the ligands, which indicates that both chelate groups of the ligands are simultaneously involved in coordination. The Ph substituents in bis(β-diketone) have a considerable effect on the composition and stability of complexes with lanthanide ions due to additional noncovalent inner-sphere interactions.

Key words: β-diketone, X-ray diffraction analysis, pH-potentiometry, complexation, lanthanides, stability constants, 1,3-bis(acetylacetonyloxy)benzene, 1,3-bis(benzoylacetonyloxy)benzene.

A large number of β-diketones containing various substituents in the α and β positions have been synthesized. These compounds can react with most metals to form complexes[1] possessing unique physicochemical properties. Lanthanide complexes with β-diketones serve as receptors for amino acids and show enantioselectivity.[2]

The composition and stability of the complexes with metal ions depend substantially on the nature of substituents, which differ in the volume and the electron-donating properties, in β-diketones. Another qualitatively different approach to the modification of the complexation properties and the design of selective extractants and chelating agents is based on the attachment of functional groups to a matrix molecule giving rise to binding centers. The nature of the matrix determines the synthetic possibilities of its functionalization and the limiting number of binding fragments, which can be attached to the matrix, provides the required balance between flexibility and rigidity of the binding centers, and is, to a large extent, responsible for the receptor properties of the molecule as a whole.

In recent years, particularly, with the development of supramolecular chemistry, numerous compounds of this type, including those with a three-dimensional architecture, have been synthesized. For example, we have studied[3,4] the influence of the nature of the carboxylate groups attached to the resorcinol, calix[4]resorcinol, pyrogallol, and calix[4]pyrogallol matrices on the efficiency and selectivity of complexation with alkali ions (Li^+, Na^+, K^+, Cs^+) and lanthanide ions (La^{3+}, Gd^{3+}, Lu^{3+}).

However, data on polydentate compounds based on β-diketones are scarce. For example, the synthesis of bis(β-diketones) of the general formulas $RCOCH_2CO—Y—COCH_2COR$ and $(RCO)(R'CO)CH—Y—CH(COR)(COR')$, where Y is the $—(CH_2)_n—$ methylene bridge ($n = 0—10$), was described.[5,6] The ligands (H_2L) of the general formula $(CH_3CO)_2CH—Y—CH(COCH_3)_2$, where Y are the rigid *n*-xylene and 2,7-naphthalenidylbis-

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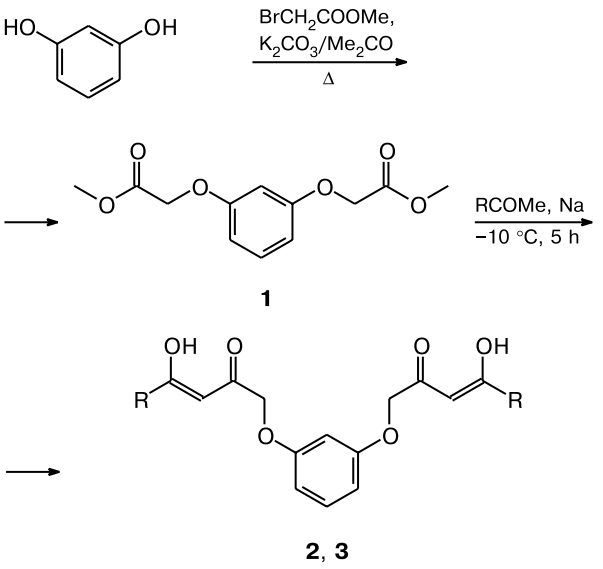
methylene bridges, were prepared. These ligands were used to synthesize[7,8] the dinuclear Cu^{II} complexes of composition Cu_2L_2, in which the metal ions are linked to each other by bis(β-diketones). The resulting complexes act as metal receptors to form *endo*- and *exo*-complexes with small nitrogen-containing molecules and heterocycles. Bis(β-diketones), in which calix[4]arene serves as the spacer Y, were also prepared.[9] These ligands also form Cu_2L_2 complexes, which act as analogous receptors for nitrogen-containing bases.

In the present study, we synthesized new bis(β-diketones), investigated their acid-base properties and complexation with lanthanide ions (La^{3+}, Gd^{3+}, Lu^{3+}), and established the structures of 1,3-bis(acetylacetonyloxy)benzene and 1,3-bis(methoxycarbonylmethoxy)benzene, which serve as the starting reagents for the synthesis of β-diketones.

Results and Discussion

We prepared bis(β-diketones) by the Claisen reaction,[10] which is one of the most widely used methods for the synthesis of β-diketones (Scheme 1).

Scheme 1



R = Me (**2**), Ph (**3**)

The reaction was carried out with 1,3-bis(methoxycarbonylmethoxy)benzene (**1**) and acetone (synthesis of compound **2**) or acetophenone (synthesis of compound **3**) in the presence of sodium metal as the condensing agent. The presence of two or more β-diketonate fragments in one molecule leads to a decrease in the yield of the final product. The yields of compounds **2** and **3** (20 and 28%, respectively) are substantially lower than the yields of 1-phenoxy-2,4-pentanedione (63%) and 4-phenoxy-1-phenyl-1,3-butanedione (70%) prepared according to an analogous procedure.[11] This fact is attributable to side reactions, which are, in particular, accompanied by the formation of acyloins[10] and ester hydrolysis.[12] This is, apparently, the reason why our attempt to synthesize analogous β-diketonate derivatives of calix[4]resorcinol by the Claisen reaction failed.

The compositions and structures of compounds **2** and **3** were confirmed by elemental analysis, ^1H and IR spectroscopy, and X-ray diffraction analysis.

Structures of compounds 1—3. The IR spectra of compounds **2** and **3**, unlike those of **1** have a complex intense absorption band at 1600 cm^{-1} (Fig. 1), which includes stretching vibrations of the double bonds of the aromatic moieties (ν(C=C)) and absorption of enolized structures.[13]

In the case of β-diketones, the keto-enol structures can occur. High intensities of the above-mentioned bands and lower ν(C=O) frequencies compared to those of ketones should be assigned to the enol structure, because the intensities of the bands of the aromatic system (ν(C=C)) are generally much weaker.[13] The spectra of compounds **2** and **3** show no evidence of an alternative diketo structure, whose bands are generally observed at 1700—1730 cm^{-1}.[13] The characteristic carbonyl absorption (ν(C=O), 1729 cm^{-1}) is exemplified in the spectrum of compound **1** (see Fig. 1). Therefore, these data suggest that in the crystals, compounds **2** and **3** exist in the enol form.

The IR spectra of the enol fragments are usually characterized also by absorption of the OH group (ν(OH)) as a broad diffuse area under the peaks ν(CH) in the 2400—3400 cm^{-1} region. In the spectra of compounds **2**

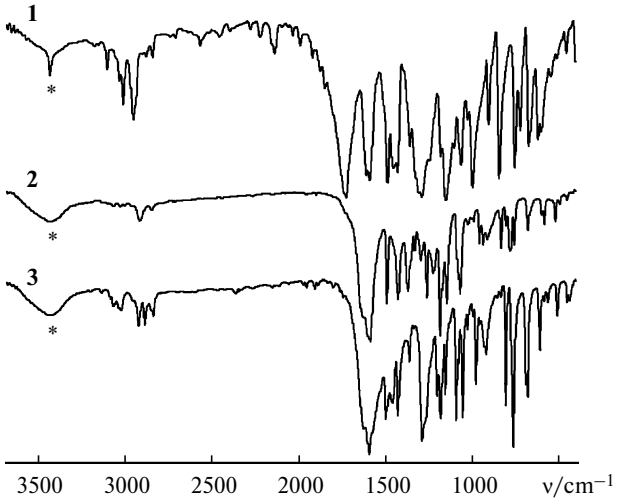


Fig. 1. IR spectra of compounds **1—3**. The absorption of the moisture from the atmosphere during sample preparation is marked with an asterisk. The spectrum of compound **1** shows a sharp peak at 3435 cm^{-1} assigned to an overtone of ν(C=O).

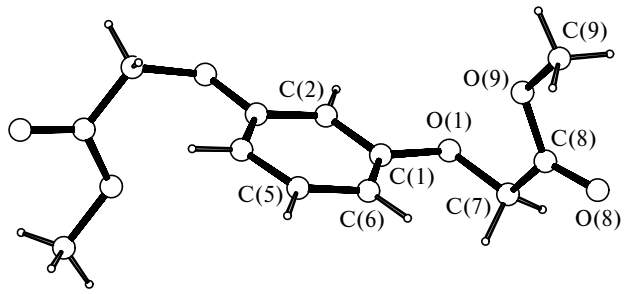


Fig. 2. Molecular structure of **1** in the crystal.

and **3**, this absorption is also observed, although it is weakly pronounced and is masked by a band of adsorbed moisture with a maximum at ~3440 cm^{-1}. In addition, the spectra of compounds **2** and **3** show a series of bands of the aromatic fragments with maxima at 3071, 3024 cm^{-1} (ν(CH)); 1501, 1431 cm^{-1} (ν(Ar)); and ~690, 766 cm^{-1} (γ(CH), γ(Ar)). The spectrum of compound **3** has an additional intense absorption band involving ν(O—C(=C)—Ph) at 1290 cm^{-1}. The spectra of both β-diketones show intense absorption bands corresponding to skeletal vibrations in the 1000—1300 cm^{-1} region. There is also an intense ν(C—O—C) band at ~1180 cm^{-1}, ν(CH_2) and ν(CH_3) bands in the 2830—2940 cm^{-1} region, and δ(CH_2) and ν(CH_3) bands in the 1360—1470 cm^{-1} region. On the whole, the IR spectroscopic data confirm that, in the crystals, compounds **2** and **3** exist in the enol form.

X-ray diffraction study of compound **1** demonstrated that molecule **1** has the C_2 symmetry (twofold axis passes through the C(2) and C(5) atoms of the benzene ring, Fig. 2). In the crystal of **2**, two independent molecules (A and B) adopt virtually identical conformations (*cf.* the torsion angles, Fig. 3). The main geometric parameters of the independent molecules are equal within the experimental error (Tables 1, 2, and 3).

Table 1. Bond lengths (*d*) in molecules **1** and **2**

Bond	*d*/Å	
	Molecule **1**	
O(1)—C(1)	1.410(8)	
O(1)—C(7)	1.456(8)	
O(8)—C(8)	1.218(8)	
O(9)—C(8)	1.357(8)	
O(9)—C(9)	1.42(1)	
C(1)—C(2)	1.387(8)	
C(1)—C(6)	1.35(1)	
C(5)—C(6)	1.383(8)	
C(7)—C(8)	1.44(1)	
	Molecule **2**	
	Molecule A	Molecule B
O(11)—C(1)	1.360(3)	1.381(3)
O(11)—C(12)	1.420(4)	1.409(3)
O(13)—C(13)	1.329(4)	1.315(3)
O(13)—H(13)	1.00(3)	0.94(4)
O(15)—C(15)	1.270(4)	1.266(3)
O(31)—C(3)	1.373(3)	1.382(3)
O(31)—C(32)	1.421(3)	1.415(3)
O(33)—C(33)	1.318(3)	1.294(4)
O(33)—H(33)	1.17(3)	1.24(3)
O(35)—C(35)	1.249(3)	1.297(4)
C(1)—C(2)	1.378(4)	1.368(4)
C(1)—C(6)	1.399(4)	1.396(4)
C(2)—C(3)	1.389(4)	1.387(4)
C(3)—C(4)	1.383(4)	1.381(4)
C(4)—C(5)	1.391(4)	1.365(4)
C(5)—C(6)	1.352(4)	1.382(5)
C(12)—C(13)	1.487(4)	1.493(4)

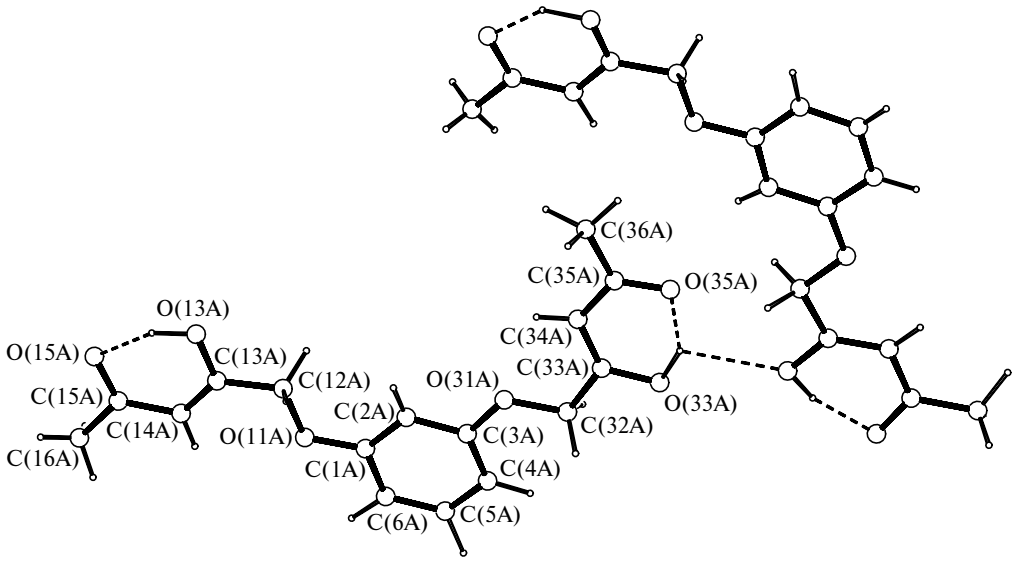


Fig. 3. Geometry of the independent molecules A and B of compound **2** and hydrogen bonds in the crystal of **2**. The atomic numbering scheme is given only for the molecule A. The H bonds are indicated by dashed lines.

Table 2. Selected bond angles (ω) in molecules **1** and **2**

Angle	ω/deg	
Molecule **1**		
C(1)—O(1)—C(7)	114.7(5)	
C(8)—O(9)—C(9)	116.9(5)	
O(1)—C(1)—C(2)	112.2(6)	
O(1)—C(1)—C(6)	125.6(6)	
C(2)—C(1)—C(6)	122.2(6)	
C(1)—C(2)—C(1′)	117.7(7)	
C(6)—C(5)—C(6′)	122.1(8)	
C(1)—C(6)—C(5)	117.9(7)	
O(1)—C(7)—C(8)	115.8(5)	
O(8)—C(8)—O(9)	120.9(6)	
O(8)—C(8)—C(7)	123.0(6)	
O(9)—C(8)—C(7)	116.0(6)	
Molecule **2**		
	Molecule A	Molecule B
C(1)—O(11)—C(12)	116.9(2)	115.9(2)
C(13)—O(13)—H(13)	105.(2)	101.(2)
C(3)—O(31)—C(32)	116.3(2)	117.0(2)
C(33)—O(33)—H(33)	104.(1)	96.(2)
O(11)—C(1)—C(2)	124.8(2)	124.2(2)
O(11)—C(1)—C(6)	115.6(2)	114.5(2)
C(2)—C(1)—C(6)	119.6(2)	121.3(3)
C(1)—C(2)—C(3)	119.6(3)	118.9(2)
O(31)—C(3)—C(2)	115.3(2)	114.2(2)
O(31)—C(3)—C(4)	123.5(2)	124.6(3)
C(2)—C(3)—C(4)	121.2(2)	121.2(3)
C(3)—C(4)—C(5)	117.7(3)	118.4(3)
C(4)—C(5)—C(6)	122.3(3)	122.4(3)
C(1)—C(6)—C(5)	119.6(3)	117.7(3)
O(11)—C(12)—C(13)	109.5(2)	109.0(2)
O(13)—C(13)—C(12)	110.1(2)	123.1(3)
O(13)—C(13)—C(14)	122.4(2)	112.4(2)
C(12)—C(13)—C(14)	127.4(3)	124.5(2)
C(13)—C(14)—C(15)	122.7(3)	120.4(2)
O(15)—C(15)—C(14)	119.8(2)	122.5(2)
O(15)—C(15)—C(16)	118.2(3)	117.4(3)
C(14)—C(15)—C(16)	122.0(3)	120.1(3)
O(31)—C(32)—C(33)	109.9(2)	109.7(2)
O(33)—C(33)—C(32)	110.9(2)	113.3(2)
O(33)—C(33)—C(34)	123.5(2)	123.0(3)
C(32)—C(33)—C(34)	125.6(2)	123.8(3)
C(33)—C(34)—C(35)	121.3(2)	121.0(3)
O(35)—C(35)—C(34)	120.8(3)	121.1(3)
O(35)—C(35)—C(36)	119.6(3)	116.9(3)
C(34)—C(35)—C(36)	119.6(2)	122.1(3)

Table 3. Selected torsion angles (τ) in molecules **1** and **2**

Angle	τ/deg	
Molecule **1**		
C(7)—O(1)—C(1)—C(2)	176.6(5)	
C(7)—O(1)—C(1)—C(6)	−6(1)	
C(1)—O(1)—C(7)—C(8)	82.2(7)	
C(9)—O(9)—C(8)—O(8)	4(1)	
C(9)—O(9)—C(8)—C(7)	179.0(7)	
O(1)—C(1)—C(6)—C(5)	−178.1(6)	
C(2)—C(1)—C(6)—C(5)	−1(1)	
O(1)—C(7)—C(8)—O(8)	176.7(6)	
O(1)—C(7)—C(8)—O(9)	1.5(9)	
Molecule **2**		
	Molecule A	Molecule B
C(12)—O(11)—C(1)—C(2)	−2.0(4)	1.9(4)
C(12)—O(11)—C(1)—C(6)	179.1(3)	−177.0(3)
C(1)—O(11)—C(12)—C(13)	−176.8(2)	−176.7(2)
H(13)—O(13)—C(13)—C(12)	178(2)	−178(2)
H(13)—O(13)—C(13)—C(14)	−3(2)	2(2)
C(32)—O(31)—C(3)—C(2)	174.3(2)	−176.5(2)
C(32)—O(31)—C(3)—C(4)	−5.3(4)	3.4(4)
C(3)—O(31)—C(32)—C(33)	−174.8(2)	−177.4(2)
H(33)—O(33)—C(33)—C(32)	170(1)	−163(1)
H(33)—O(33)—C(33)—C(34)	−10(1)	18(2)
O(11)—C(12)—C(13)—O(13)	178.4(2)	−179.8(2)
O(11)—C(12)—C(13)—C(14)	−0.2(4)	0.6(4)
O(13)—C(13)—C(14)—C(15)	0.2(5)	2.3(4)
C(12)—C(13)—C(14)—C(15)	178.6(3)	−178.1(3)
C(13)—C(14)—C(15)—O(15)	−1.8(5)	−0.1(5)
C(13)—C(14)—C(15)—C(16)	179.3(3)	178.2(3)
O(31)—C(32)—C(33)—O(33)	−173.2(2)	−176.3(2)
O(31)—C(32)—C(33)—C(34)	7.1(4)	3.3(4)
O(33)—C(33)—C(34)—C(35)	2.0(4)	−1.2(5)
C(32)—C(33)—C(34)—C(35)	−178.3(3)	179.2(3)
C(33)—C(34)—C(35)—O(35)	−2.5(4)	−0.4(5)
C(33)—C(34)—C(35)—C(36)	177.2(3)	−179.2(3)

Molecule **1** is nonplanar. The methoxycarbonyl groups deviate from the plane of the benzene ring due to a twist about the O(1)—C(7) bond (C(1)—O(1)—C(7)—C(8), 82.2(7)°). The ester substituent is planar (O(1)—C(7)—C(8)—O(9), 1.5(9)°; C(9)—O(9)—C(8)—C(7), 179.0(7)°). Since the molecule has the C_2 symmetry, the substituents are located on the opposite sides of the plane of the benzene ring. This conformation is unfavorable for stacking interactions between the benzene rings in the crystal, and the crystal packing of **1** is determined by C—H...O interactions between the methylene groups and the carbonyl oxygen atom (C(7)—H(71)...O(8′) (1/2 + *x*, 1/2 − *y*, −*z*), C—H, 1.02 Å; H...O, 2.41 Å; C...—O, 3.38(1) Å; C(7)—H(71)...O(8′), 160°) and C—H...π interactions between the C(9) atom of the Me group and the benzene ring of the adjacent molecule (*x* − 1, *y*, *z*) (Fig. 4). The C—H...π interactions are characterized by the following parameters: C(9)—H(91), 0.91 Å; H(91)—Cg(1), 2.73 Å; C(9)—Cg(1), 3.493 Å; C(9)—H(91)—Cg(1), 137°, where Cg(1) is the center of the benzene ring.

In the crystal, molecules **2**, unlike molecule **1**, are planar (maximum deviations of the atoms from the mean plane are 0.2 Å). The planar acetylacetonate substituents are located unsymmetrically relative to the benzene ring: the C(1)—C(2) and O(11)—C(12) bonds have the *cis* conformation relative to the C(1)—O(11) bond, whereas the C(2)—C(3) and O(31)—C(32) bonds are in the *trans* con-

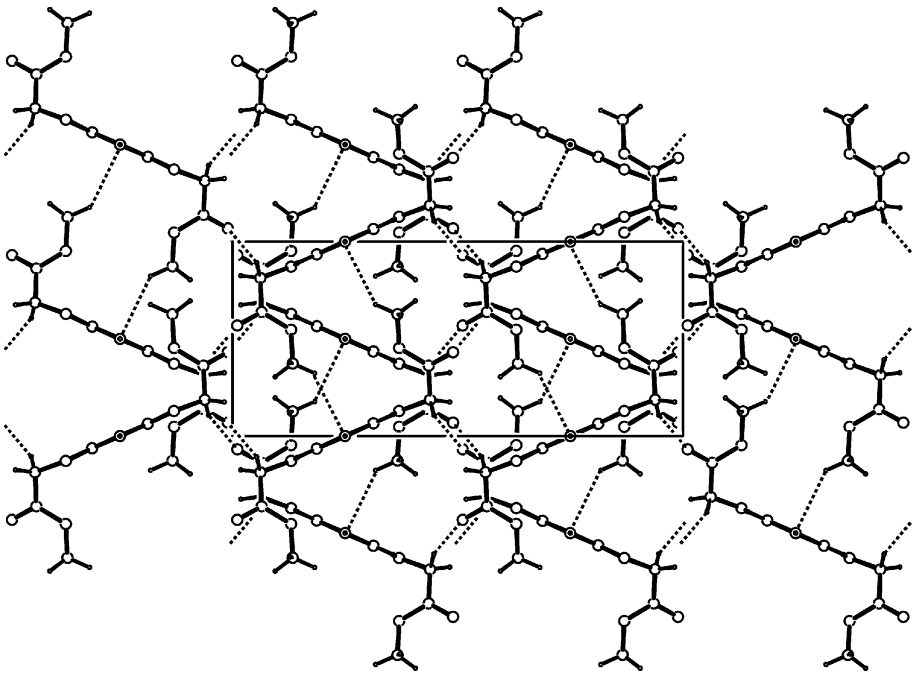


Fig. 4. Crystal packing of **1** projected along the 0*y* axis. The C—H...O and C—H...π-type intermolecular contacts are indicated by dashed lines.

formation relative to the C(3)—O(31) bond (see Fig. 3). As expected, the planar conformation of the acetylacetonate substituents is stabilized by intramolecular hydrogen bonding. The parameters of the intramolecular hydrogen bonds are as follows: O(13A)—H(13A)...O(15A), O—H, 0.99(3) Å; H...O, 1.64(3) Å; O...O, 2.538(3) Å; the O—H...O angle is 149(3)°; O(33A)—H(33A)...O(35A), O—H, 1.16(3) Å; H...O, 1.53(3) Å; O...O, 2.556(3) Å; the O—H...O angle is 142(3)°; O(13B)—H(13B)...O(15B), O—H, 0.95(3) Å; H...O, 1.65(3) Å; O...O, 2.542(3) Å; the O—H...O angle is 156(3)°; O(33B)—H(33B)...O(35B), O—H, 1.24(3) Å; H...O, 1.41(3) Å; O...O, 2.524(3) Å; the O—H...O angle is 145(2)°. The independent molecules A and B are linked to each other by the intermolecular O(33A)—H(33A)...O(13B′) hydrogen bond (1 – *x*, 2 – *y*, 1 – *z*) (O—H, 1.16(3) Å; H...O, 2.42(3) Å; O...O, 2.991(3) Å; the O—H...O angle is 108(2)°). The parameters of this bond show that it is much weaker than the intramolecular bonds in the acetylacetonate fragments of the molecules. The hydrogen bond network in the crystal of **2** is shown in Fig. 3.

In the crystal of **2**, there are also shortened contacts between the benzene rings of the adjacent molecules, which are consistent with the criterion of stacking interactions (distances between the planes of the rings are 3.005 and 3.536 Å). On the whole, the crystal packing of **2** can be described as a layer packing (Fig. 5).

Acid-base properties of bis(β-diketones) 2 and 3 and their complexation with lanthanide ions. The deprotonation constants of β-diketones **2** and **3** are of the same order of magnitude, although the presence of the Me substituents facilitates dissociation of molecule **2** (pK_1 = 8.16±0.02, pK_2 = 17.50±0.05) compared to molecule **3** (pK_1 = 8.38±0.01, pK_2 = 17.99±0.02). The constants pK for acetylacetone and benzoylacetone determined under analogous conditions are virtually equal (pK = 9.47±0.03 and 9.56±0.03, respectively). The fact that the acidities of

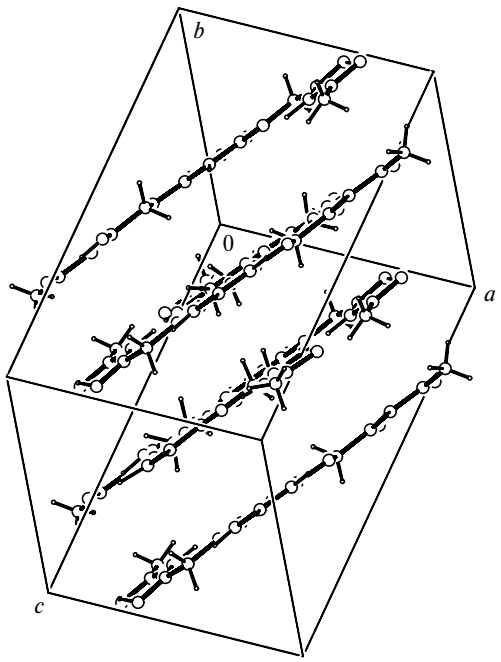


Fig. 5. Crystal packing of **2**.

β-diketones **2** and **3** are higher than those of acetylacetone and benzoylacetone indicates that the enol form is stabilized in aqueous-ethanolic solutions.

The presence of lanthanide ions in the lanthanide ion : ligand concentration ratios of 1 : 1 and 1 : 2 substantially facilitates the first and second steps of dissociation of β-diketones **2** and **3**, which is evidence for the formation of the corresponding complexes. For Lu and Gd, the titration curves of ligand **2** at the ratio of 1 : 1 are substantially different from those measured at the ratio of 1 : 2, but these curves are similar in the case of La (Fig. 6, *a*). Actually, at the concentration ratio of 1 : 2, accumulation of the complexes with $m = 2$, $n = 1$, $k = 2$—4 was observed for all the ions under consideration. In the region of accumulation of the complex with $m = 2$, $n = 1$, $k = 3$ (Fig. 7), the solution became turbid due, apparently, to precipitation of this electroneutral complex. A further increase in pH leads to complete dissolution of the precipitate due to its transformation into the charged complex with $m = 2$, $n = 1$, $k = 4$. However, the presence of Lu^{3+} and Gd^{3+} in the equimolar metal ion : ligand ratio gives rise mainly to charged soluble complexes with the stoichiometry $m = 1$, $n = 1$, $k = 1$—2, whereas complexes with $m = 2$, $n = 1$, $k = 2$—4 are predominantly formed in the case of lanthanum. Because of this, turbidity of a solution containing lanthanum ions in the region of accumulation of the complex with $m = 2$, $n = 1$, $k = 3$ and dissolution of this complex due to its transformation into the complex with $m = 2$, $n = 1$, $k = 4$ are observed at the ratios of 1 : 1 and 1 : 2, respectively. A noticeable increase in stability of the complex with $m = 1$, $n = 1$, $k = 2$ compared to the complex with $m = 1$, $n = 1$, $k = 1$ suggests that both diketonate fragments are involved in coordination to lanthanide ions. An analogous, though less substantial, increase in stability is also observed with increasing degree of deprotonation of the complexes with $m = 2$, $n = 1$ as k changes from 2 to 3 and 4.

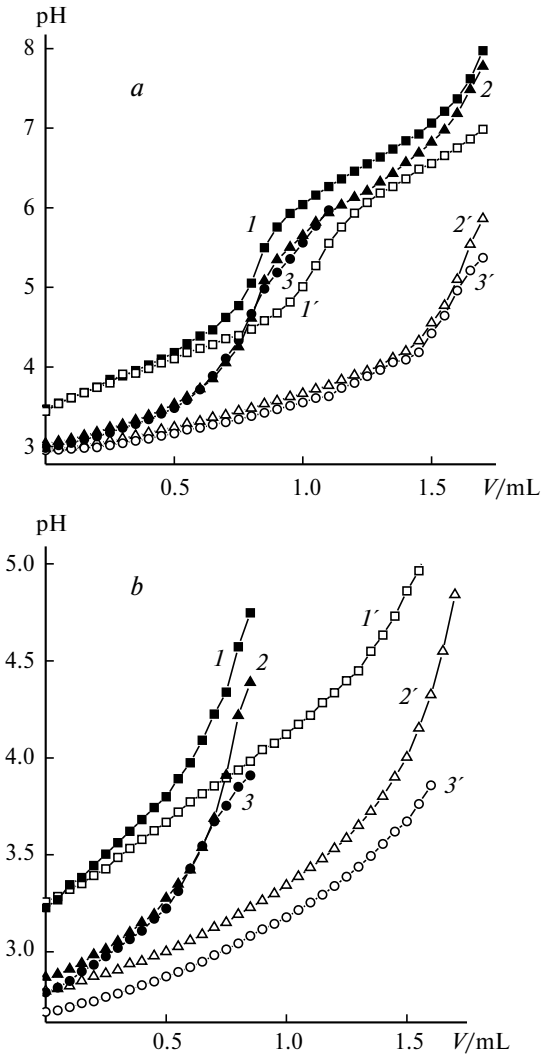


Fig. 6. The pH-potentiometric titration curves for compounds **2** (*a*) and **3** (*b*) in the presence of Ln^{3+}: La^{3+} (*1*, *1′*), Gd^{3+} (*2*, *2′*), and Lu^{3+} (*3*, *3′*) at the ligand to Ln^{3+} ratios of 1 : 1 and 1 : 2, respectively.

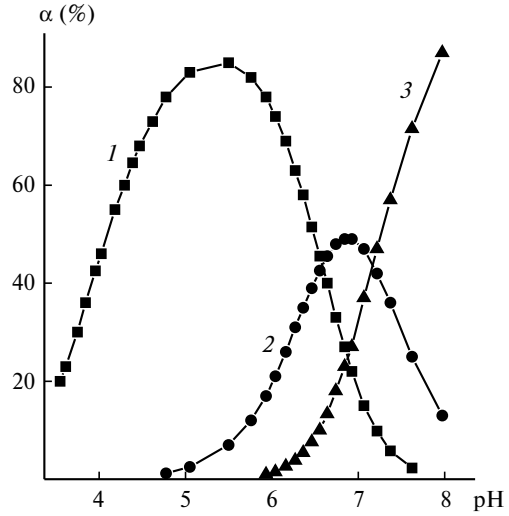


Fig. 7. The pH dependence of the degree of accumulation of the complexes in solution for the ligand **2**—La^{3+} system (**2** : La^{3+} ratio is 2 : 1). The complex forms: $m = 2$, $n = 1$, $k = 2$ (*1*); $m = 2$, $n = 1$, $k = 3$ (*2*); $m = 2$, $n = 1$, $k = 4$ (*3*).

The titration curves of ligand **3** measured at the metal : ligand ratio of 1 : 1 differ substantially from those measured at the ratio of 1 : 2 for all the ions under consideration (Fig. 6, *b*). However, in contrast to ligand **2**, precipitation is observed at the ratios of 1 : 1 and 1 : 2 upon the addition of ~1.5 equiv. of an alkali per mole of the ligand and the addition of one mole of an alkali, respectively. Taking into account the electroneutrality of the precipitate that formed and the number of equivalents of the alkali required for precipitation, the most probable stoichiometry of the precipitates is 213 and 313, respectively.

Table 4. Stability constants (logβ, β/L mol^{-1}) of the complexes with β-diketones **2** and **3** $\{([H_{2-k/m}L]^{k/m-})_m(Ln^{3+})_n\}^{3n-k}$ formed in the H_2L—Ln^{3+} system

Ln^{3+}	m	n	k	logβ		$\Delta\log\beta_{Ln/La}$	
				2	**3**	**2**	**3**
La^{3+}	2	1	2	13.8±0.02	15.1±0.04	—	—
	2	1	3	16.7±0.12	20.6±0.05	—	—
	2	1	4	18.8±0.14	25.3±0.1	—	—
	3	1	3	—	23.17±0.2	—	—
Gd^{3+}	1	1	1	8.2±0.1	—	—	—
	1	1	2	14.16±0.07	—	—	—
	2	1	2	15.8±0.06	—	2.0	—
	2	1	3	19.2±0.2	23.6±0.03	2.5	3.0
	2	1	4	21.9±0.25	28.8±0.1	3.1	3.5
	3	1	3	—	26.32±0.2	—	—
Lu^{3+}	1	1	1	8.3±0.2	—	—	—
	1	1	2	13.87±0.07	—	—	—
	2	1	2	16.0±0.06	—	2.2	—
	2	1	3	19.3±0.27	24.4±0.03	2.6	3.8
	2	1	4	—	30.2±0.04	—	4.9
	3	1	3	—	27.52±0.17	—	—

Simulation of pH-potentiometric data at the ratio of 1 : 1 showed a better goodness-of-fit criterion (F = 0.1—0.2) for a model, which includes complexes with m = 2, n = 1, k = 2—3, than for a model, which includes complexes with m = 1, n = 1, k = 1—2 (F = 1—1.5), which is consistent with the stoichiometry of the precipitate that formed. At the ratio of 1 : 2, the model, which includes the complex with m = 3, n = 1, k = 3, also provides a better goodness-of-fit to the experimental data. The stability constants (logβ) for the complexes with β-diketones **2** and **3** are given in Table 4.

When analyzing the stability constants given in Table 4, it should be noted that the stoichiometry of the complexes changes in going from ligand **2** to **3**. In the case of ligand **3**, the formation of complexes with m = 1, n = 1 was not observed in the concentration conditions under consideration. This is most likely attributable to higher stability of complexes with m = 2, n = 1, k and ligand **3** compared to the corresponding complexes with ligand **2**. At the metal : ligand concentration ratio of 1 : 2, the complex with m = 3, n = 1, k = 3 becomes the major one as the concentration of ligand **3** increases further.

Therefore, the complexes with m = 2, n = 1, k = 2—3 and m = 3, n = 1, k = 3 and ligand **3** are additionally stabilized compared to the corresponding complexes with ligand **2**. Taking into account small differences in the acidity of the ligands under question and the identity of the coordination unit to which the metal ion is coordinated, it is reasonable to suggest that the complexes with m = 2, n = 1, k and m = 3, n = 1, k = 3 are additionally stabilized most likely due to noncovalent inner-sphere interactions, *viz.*, stacking and CH—π interactions between the aromatic fragments of coordinated ligands.[14,15] Interestingly, the stability substantially increases in going from ligand **2** to **3** as the degree of deprotonation of the complex with m = 2, n = 1, k increases. In particular, the stability of the complex with m = 2, n = 1, k = 4 increases by approximately seven orders of magnitude in going from ligand **2** to **3**, whereas the analogous increase for the complex with m = 2, n = 1, k = 2 is smaller than three orders of magnitude. Consequently, the involvement of both diketonate fragments in coordination to the lanthanide ion in the complex with m = 2, n = 1, k = 4 provides conditions for more efficient inner-sphere interactions compared to the complex with m = 2, n = 1, k = 2, in which only one diketonate fragment of each ligand is involved in inner-sphere coordination to the lanthanide ion. The possible structural models of the lanthanide complexes with m = 2, n = 1, k = 4 and ligands **2** and **3** are shown in Fig. 8.

The stability constants of the complexes with c m = 2, n = 1 increase with increasing atomic number of the lanthanide in the series La < Gd ≤ Lu, which is typical of lanthanide complexes with chelating agents, in which a rigid preorganization of the donor centers is absent.[16] An increase in the degree of deprotonation k of the complexes with m, n, k and ligands **2** and **3** leads to an increase in selectivity of complexation ($\Delta\log\beta_{La/Lu} = \log\beta_{Ln} - \log\beta_{La}$, where β are the stability constants of the com-

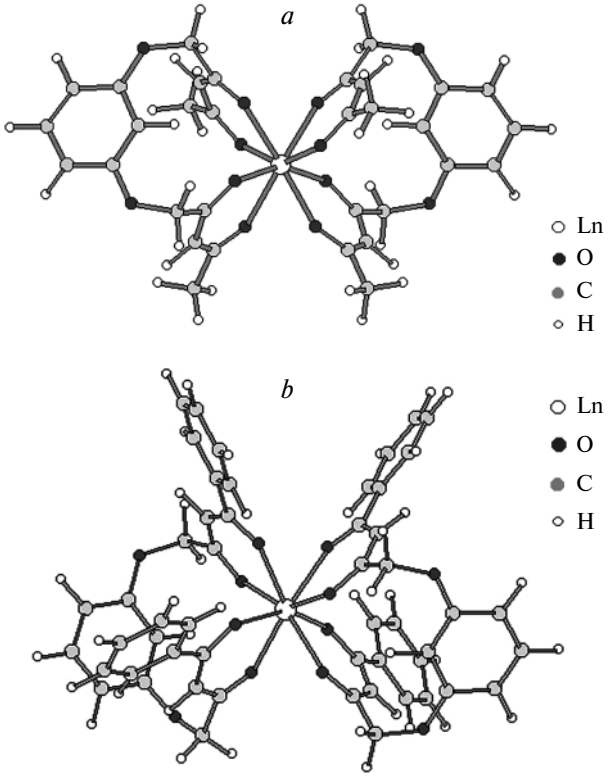


Fig. 8. Structural models of the complexes of lanthanide ions with ligands **2** (*a*) and **3** (*b*) with m = 2, n = 1, k = 4.

plexes). The maximum value of $\Delta\log\beta_{Lu/La}$ becomes as high as 4.9 logarithmic units for the complex with $m = 2$, $n = 1$, $k = 4$ and β-diketone **3** in going from La^{3+} to Lu^{3+}. Consequently, the positive charge density of the central ion is the decisive factor responsible for stability of the octadentate coordination of two dideprotonated bis(β-diketones) to the lanthanide ion.

To summarize, the results of X-ray diffraction study, IR spectroscopic data, and higher acidities of β-diketones **2** and **3** compared to acetylacetone and benzoylacetone provide evidence that the enol form is stabilized both in the crystalline state and aqueous-ethanolic solutions. The high complexation ability of ligands **2** and **3** is associated with the presence of two diketonate fragments in the ligand molecule. The stability of the resulting lanthanide complexes increases with increasing atomic number of the lanthanide (La < Gd ≤ Lu). An increase in the degree of deprotonation of bis(β-diketones) also leads to an increase in the constants and selectivity of complexation. The structure of the ligands, in particular, the presence of aromatic substituents, has a considerable effect on the composition and stability of the complexes with lanthanide ions due to the occurrence of additional noncovalent inner-sphere interactions.

Experimental

1,3-Bis(methoxycarbonylmethoxy)benzene was prepared according to a procedure described in the literature.[17] Commercial KOH (analytical grade) and lanthanide chlorides (analytical grade) were used; bidistilled water was used. Ethanol was additionally purified according to a standard procedure.[18] Toluene, Me_2CO, and acetophenone were purified by distillation over Na, P_2O_5, and $CaCl_2$, respectively. The starting organic reagents, *viz.*, resorcinol, methyl bromoacetate (Aldrich), and sodium metal, were used without additional purification.

The ^{1}H NMR spectra were recorded on a Bruker DRX-300 instrument operating at 300 MHz; the chemical shifts were measured in the δ scale using Me_4Si as the internal standard. The IR spectra were recorded on a Bruker Vector-22 Fourier-transform IR spectrometer at 4-cm^{-1} resolution; 16 scans were accumulated. The melting points were determined on a Boetius melting-point microapparatus. The purities of the compounds were controlled by TLC. The geometry of the structural models of the complexes of lanthanide ions with ligands **2** and **3** was optimized by the molecular mechanics method (MM+)[19] incorporated in the HyperChem7.03 program package.[20]

X-ray diffraction analysis. Crystals of **1** are orthorhombic; the crystals were grown by crystallization from toluene, $C_{12}H_{14}O_6$, m.p. 57 °C. At 20 °C, $a = 7.591(3)$ Å, $b = 9.059(5)$ Å, $c = 17.556(9)$ Å, $V = 1207(1)$ Å^3, $Z = 4$, $d_{calc} = 1.40$ g cm^{-3}, space group *Pbcn* (molecule occupies a special position on a twofold axis). The unit cell parameters and intensities of 1117 reflections, of which 504 reflections were with $I \geq 3\sigma$, were measured on an automated four-circle Enraf-Nonius CAD-4 diffractometer (λ-Mo-Kα, graphite monochromator, ω/2θ scanning technique, $\theta \leq 26.9°$).

Crystals of **2** are triclinic, $C_{12}H_{18}O_6$, the crystals were grown by crystallization from hexane, m.p. 56—58 °C. At 20 °C, $a = 9.207(2)$ Å, $b = 10.202(4)$ Å, $c = 16.557(9)$ Å, $\alpha = 97.62(4)°$, $\beta = 91.84(3)°$, $\gamma = 98.44(3)°$, $V = 1523(2)$ Å^3, $Z = 4$, $d_{calc} = 1.45$ g cm^{-3}, space group $P\bar{1}$ (two independent molecules A and B). The unit cell parameters and intensities of 6439 reflections, of which 3789 reflections were with $I \geq 3\sigma$, were measured on an automated four-circle Enraf-Nonius CAD-4 diffractometer (λ-Cu-Kα, graphite monochromator, ω/2θ scanning technique, $\theta \leq 76°$).

The intensities of three check reflections showed no decrease in the course of X-ray data collection. The absorption correction was ignored (μMo = 1.06 (**1**) and μCu = 8.64 (**2**) cm^{-1}). The structures were solved by direct methods using the SIR program[21] and refined first isotropically and then anisotropically. The positions of the hydrogen atoms were revealed from difference electron density maps. In the structure of **1**, the contributions of these atoms to the structure factors were taken into account with fixed positional and isotropic temperature parameters. In the structure of **2**, the hydrogen atoms were refined isotropically in the final step. The final R factors were as follows: for the structure **1**, $R = 0.093$, $R_w = 0.105$ for 429 independent reflections with $F^2 \geq 3\sigma$; for the structure of **2**, $R = 0.054$, $R_w = 0.062$ for 2990 independent reflections with $F^2 \geq 3\sigma$. All calculations were carried out using the MOLEN program package [22] on an AlphaStation 200. Intermolecular interactions were analyzed and the figures of the structures were drawn using the PLATON program.[23]

The molecular structures of **1** and **2** are shown in Figs 2 and 3, respectively. Selected geometric parameters are given in Tables 1—3. The atomic coordinates, details of X-ray data collection, and parameters of structure solution and refinement were deposited with the Cambridge Structural Database (CCDC refcodes 251796 and 251797)*.

pH-Potentiometry. Titration was carried out with a KOH solution at a concentration of $1.36 \cdot 10^{-2}$ mol L^{-1} in a H_2O—EtOH mixture (80 vol.%) on an I-130 instrument with an accuracy of 0.05 pH units at 40±1 °C. The acidity in the H_2O—EtOH mixture (80 vol.%) was determined using a procedure,[24,25] according to which the ion meter was calibrated against standard buffer solutions in water, and then the electrode was soaked in the H_2O—EtOH mixture (80 vol.%) for 1 day before performing pH measurements of aqueous-organic solutions. The values of pH in aqueous-organic solutions were determined from the equation

$$pH = pH_{exp} - \Delta pH,$$

where pH_{exp} is the measured pH in a mixed solvent and ΔpH is the difference between the activities of protons in aqueous and aqueous-organic solutions.

The values of ΔpH were determined by measuring pH of solutions containing hydrochloric acid at different concentrations in a mixed solvent (pH_{w+s}) and water (pH_w) from the following equation:

$$\Delta pH = pH_{w+s} - pH_w.$$

* These data can be obtained, free of charge, on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Tel.: +44 (122 3) 76 2910, fax: +44 (122 3) 33 6033. E-mail: deposit@ccdc.cam.ac.uk.

The solutions were titrated at the lanthanide : ligand ratios of 1 : 1 and 1 : 2 in the pH range of 2.5—8. For the free ligands, the solutions were titrated to pH 12 at the ligand concentrations of $2 \cdot 10^{-3}$ and $4 \cdot 10^{-3}$ mol L^{-1}. The composition of the mixed solvent, the concentrations, and the temperature for titration were chosen so as to provide satisfactory solubility of the starting components and reaction products.

The experimental data were processed using the CPESSP program.[26] For the chosen basic species (H_2L is ligand **2** or **3**, the lanthanide ion Ln^{3+}), the following reaction equations were derived

$$H_2L \rightleftharpoons HL^- + H^+, \quad (1)$$

$$H_2L \rightleftharpoons L^{2-} + 2\,H^+, \quad (2)$$

$$m\,H_2L + n\,Ln^{3+} \rightleftharpoons \{([H_{2-k/m}L]^{k/m-})_m(Ln^{3+})_n\}^{3n-k} + k\,H^+, \quad (3)$$

which are characterized by the equilibrium constants.

In accordance with Eq. (3), the stoichiometry of the $\{([H_{2-k/m}L]^{k/m-})_m(Ln^{3+})_n\}^{3n-k}$ complexes is denoted as (m, n, k), where m is the amount of the ligand anions $[H_{2-k}L]^{k-}$ involved in the reaction, n is the amount of the cations, and k is the amount of the protons being abstracted. The mathematical model is described by Eqs (1)—(3). The dissociation and complexation constants ($\beta_{i...q}$) corresponding to the minimum of the Fisher functional (Eq. (4)) were calculated by an iteration procedure using the CPESSP program. The reliability of the model was evaluated by the Fisher criterion (Eq. (5)).

$$F = \Sigma[(\tilde{n}_{exp} - \tilde{n}_{calc})w_m]^2, \quad (4)$$

$$F_{min} \le F\sigma^2(N - 2k), \quad (5)$$

where $\tilde{n}_{exp}$ and $\tilde{n}_{calc}$ are the experimental and calculated Bjerrum functions, respectively, N is the number of experimental points, k is the number of approximated equilibria, w_m is the rms error for the mth experimental point, and σ^2 is the rms deviation.

The model, which adequately described the experimental data under particular concentration conditions (ligand concentration was $2 \cdot 10^{-3}$ mol L^{-1}, the metal : ligand concentration ratios were 1 : 1 and 1 : 2), was validated in other concentration conditions (ligand concentration was $4 \cdot 10^{-3}$ mol L^{-1}, the metal : ligand concentration ratios were 1 : 1 and 1 : 2). This validation allowed us to refine the stoichiometry of the complexes, in particular, made it possible to decide between the complexes with $m = 1$, $n = 1$, k and $m = 2$, $n = 2$, k or the complexes with $m = 1$, $n = 1$, k and $m = 2$, $n = 1$, k.

1,3-Bis(acetylacetonyloxy)benzene (2). A mixture of ester **1** (5.1 g, 0.02 mol) and Me_2CO (5.9 mL, 0.08 mol) was added dropwise with stirring to a suspension prepared from sodium (2 g, 0.087 mol) in anhydrous toluene (50 mL) under argon at −10 °C for 2 h. The reaction mixture was kept at this temperature for 2 h. Then cooling was terminated and the mixture was stirred until it was warmed to room temperature (~20 °C). The reaction mixture was separated from residual sodium by decantation, and dry diethyl ether (50 mL) was added. The sodium salt that precipitated was filtered off, thoroughly washed with diethyl ether, and suspended in dichloromethane (100 mL). Then a 10% hydrochloric acid was added with vigorous stirring until the salt was completely dissolved. The solvent was separated and dried with $MgSO_4$. The solvent was distilled off *in vacuo*. The residue was purified by column chromatography on silica gel using a hexane—EtOAc mixture as the eluent (20 vol.%). The product was additionally recrystallized from hexane. Compound **2** was obtained in a yield of 1.24 g (20%) , m.p. 56—58 °C. Found (%): C, 62.96; H, 6.13. $C_{16}H_{18}O_6$. Calculated (%): C, 62.74; H, 5.92. ^{1}H NMR ($CDCl_3$), δ: 2.10 (s, 6 H, COMe); 4.56 (s, 4 H, OCH_2); 5.88 (s, 2 H, CH); 6.4—6.6 (m, 3 H, Ar); 7.21 (t, 1 H, Ar, J = 8.14 Hz); 15.23 (s, 2 H, OH). The ^{1}H NMR spectrum shows signals for the protons of the ketone form at the 5% level: 2.28 (s, 6 H, COMe); 4.60 (s, 4 H, OCH_2).

1,3-Bis(benzoylacetonyloxy)benzene (3) was synthesized analogously to compound **2** starting from sodium (2 g, 0.087 mol), ester **1** (5.1 g, 0.02 mol), and acetophenone (9.4 mL, 0.08 mol). The product was purified by double recrystallization from MeOH. Compound **3** was obtained in a yield of 2.4 g (28%), m.p. 112—114 °C. Found (%): C, 72.71; H, 5.37. $C_{26}H_{22}O_6$. Calculated (%): C, 72.55; H, 5.15. ^{1}H NMR ($CDCl_3$), δ: 4.68 (s, 4 H, OCH_2); 6.4—6.7 (m, 4 H, Ar, 1 H, CH); 7.2—7.3 (m, 1 H, Ar); 7.4—7.6 (m, 6 H, Ar); 7.6—7.8 (m, 4 H, Ar); 15.90 (s, 2 H, OH). The ^{1}H NMR spectrum shows a signal for the protons of the ketone form at the 5% level: 4.26 (s, 4 H, OCH_2).

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