Quantum-chemical and spectroscopic studies of structures of 1 : 2 complexes of carbonyl compounds with aluminum halides*

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Quantum-chemical calculations of model systems, namely, benzaldehyde and its 1 : 1 and 1 : 2 complexes with $AlCl_3$, were carried out by the MNDO method. In the 1 : 2 complex, a bridging Al—Cl—Al bond occurs. Apparently, this complex is stabilized through the Coulomb interaction between the positively charged C atom of the carbonyl group and the $AlCl_3$ fragment, which carries an excessive negative charge and which is not involved in donor-acceptor bonding with the carbonyl O atom. The IR spectra of the 1 : 1 and 1 : 2 complexes of benzophenone with $AlBr_3$ were recorded, and the differences in the low-frequency regions of these spectra, which are indicative of the presence of the $Br_2Al—Br—AlBr_3$ fragment in the 1 : 2 complex, are discussed.

Key words: aluminum chloride, aluminum bromide, carbonyl compounds, 1 : 1 and 1 : 2 complexes, quantum chemical calculations; IR spectra.

Previously, we have demonstrated that ketones and aldehydes of the benzene, thiophene, and furan series form not only the well-known 1 : 1 complexes with aluminum halides AlX_3 (X = Cl or Br), but also complexes which contain two acceptor molecules per donor molecule.[1—5] It should be noted that only 1 : 1 complexes of aliphatic ketones were observed by calorimetric, dielectrometric, and cryoscopic titration methods.[2] The suggestion that the second AlX_3 molecule is bonded to the aromatic system of the donor molecule with the formation of a πv complex was not confirmed by the analysis[5] of the UV spectrum of the complex of benzophenone with $AlBr_3$. Based on the analysis[4] of the ^{13}C NMR spectra of the complexes of some aromatic ketones with aluminum chloride and aluminum bromide, the structures of 1 : 2 molecular compounds were suggested. The most important structural feature suggested[4] based on the indirect evidence is a partial retention of the bridge typical of the aluminum halide dimer.

In this work, we carried out quantum-chemical studies of model 1 : 1 and 1 : 2 complexes of benzaldehyde with $AlCl_3$. We also attempted to interpret the low-frequency bands in the IR spectra of the analogous complexes of benzophenone with $AlBr_3$.

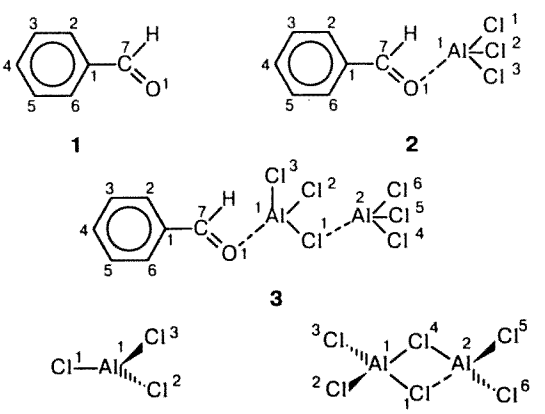
Calculation Procedure and Experimental

Calculations of the PhCHO molecule (**1**), the $PhCHO \cdot AlCl_3$ (**2**) and $PhCHO \cdot 2AlCl_3$ (**3**) complexes, $AlCl_3$, and Al_2Cl_6 were carried out on an IBM PC 486 computer by the conventional semiempirical MNDO method[6] with full optimization of the geometry.

The IR spectra were recorded on a Perkin—Elmer 577 instrument in the 500—200 cm^{-1} region (Nujol mulls) with the use of cells with polyethylene windows. With the aim of preparing complexes **2** and **3**, anhydrous aluminum bromide (analytical grade) and benzophenone (reagent grade), which was additionally purified by recrystallization, m.p. 48 °C (from aqueous ethanol), were weighed with protection from atmospheric moisture and mixed in stoichiometric ratios (1 : 1 or 1 : 2) in a flask with a ground stopcock. Heat evolution was observed, and the mixtures liquefied. Vaseline oil was added to the complex obtained, and the mass was homogenized by gentle heating.

Results and Discussion

The results of the MNDO calculations for the optimized structures of **1**—**3** and of the $AlCl_3$ and Al_2Cl_6 molecules are given in Tables 1 and 2.



1 **2**

3

* This article is dedicated to Academician M. G. Voronkov on the occasion of his 75th birthday.

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Table 1. Results of the quantum-chemical MNDO calculations of benzaldehyde (**1**) and its 1 : 1 (**2**) and 1 : 2 (**3**) complexes with $AlCl_3$

Parameter	**1**	**2**	**3**	$AlCl_3$	Al_2Cl_6
Enthalpy of formation, Δ_fH/kcal mol^{-1}	−9.6	−316.6	−325.8	−140.7	−295.9
Ionization potential, *IP*/eV	9.7	10.7	11.0	13.1	13.1
Difference in the orbital energies of LUMO and HOMO, $\Delta E_{f\to v}$/eV	9.2	8.4	8.3	11.0	10.4
Dipole moment, μ/D	2.8	11.9	12.3	0	0
Charges on atoms, *Q*/*e*:					
C(CO)	0.31	0.46	0.51		
H(CHO)	0.01	0.07	0.08		
O(CO)	−0.30	−0.33	−0.39		
Al(1)	—	0.94	1.04	0.99	0.97
Al(2)	—	—	0.94		0.97
Cl(1)	—	−0.42	−0.38	−0.33	−0.32
Cl(2)	—	−0.42	−0.38	−0.33	−0.32
Cl(3)	—	−0.42	−0.38	−0.33	−0.33
Cl(4)	—	—	−0.43		−0.32
Cl(5)	—	—	−0.41		−0.32
Cl(6)	—	—	−0.35		−0.33
C(1)	−0.17	−0.22	−0.24		
C(2)	0.01	0.06	0.06		
C(6)	−0.01	0.03	0.05		
C(3)	−0.08	−0.09	−0.09		
C(5)	−0.08	−0.09	−0.09		
C(4)	−0.02	0.02	0.04		
H(Ar)	0.07	−0.08	−0.08		

Table 2. Geometric parameters of the benzaldehyde molecule (**1**), the $PhCHO \cdot AlCl_3$ (**2**) and $PhCHO \cdot 2AlCl_3$ (**3**) complexes, the $AlCl_3$ monomer, and the Al_2Cl_6 dimer calculated by the MNDO method

Parameter	**1**	**2**	**3**	$AlCl_3$	Al_2Cl_6
Bond length, *d*/Å:					
C(1)—C(7)	1.49	1.47	1.47	—	—
C(7)—H(7)	1.11	1.12	1.11	—	—
C(7)—O(1)	1.22	1.25	1.25	—	—
O(1)—Al(1)	—	1.82	1.80	—	—
Al(1)—Cl(2)	—	2.10	2.10	2.06	2.07
Al(1)—Cl(1)	—	—	2.24	—	2.28
Al(2)—Cl(1)	—	—	2.36	—	2.28
Bond angle, ω/deg:					
C(1)—C(7)—O(1)	125	123	123	—	—
C(7)—O(1)—Al(1)	—	145	159	—	—
O(1)—Al(1)—Cl(2)	—	104	106	—	—
O(1)—Al(1)—Cl(1)	—	—	107	—	—
Al(1)—Cl(1)—Al(2)	—	—	122	—	86
Cl(2)—Al(1)—Cl(3)	—	115	119	120	122
Torsion angle, φ/deg:					
C(2)—C(1)—C(7)—O(1)*	0	−6	−7	—	—
H(7)—C(7)—O(1)—Al(1)	—	0	−5	—	—
C(7)—O(1)—Al(1)—Cl(1)	—	60	64	—	—
O(1)—Al(1)—Cl(1)—Al(2)	—	—	17	—	—
Al(1)—Cl(1)—Al(2)—Cl(4)	—	—	58	—	0

* The dihedral angle between the planes of the benzene ring and the CHO group.

The models of complexes **2** and **3** constructed with the use of the MOLDRAW program[7] using the atomic coordinates of the corresponding structures, which were calculated by the MNDO method with energy minimization, are shown in Fig. 1.

It should be emphasized that we failed to optimize the geometric parameters of the 1 : 2 structure, in which one acceptor molecule is bonded to the carbonyl O atom in the fashion observed for the nv complex (*i.e.*, analogously to the 1 : 1 complex), and the second molecule is bonded as in a πv complex: the energy minimum corresponding to such a donor-acceptor form was not observed on the potential energy surface. This agrees with the results[5] obtained by the analysis of the UV spectrum of the complex of benzophenone with $AlBr_3$.

The results of our quantum-chemical calculations demonstrated that the transition from the free PhCHO molecule to the $PhCHO \cdot AlCl_3$ and $PhCHO \cdot 2AlCl_3$ complexes is accompanied by a slight shortening of the C(1)—CHO bond (from 1.49 to 1.47 Å) and a slight elongation of the C=O bond (from 1.22 to 1.25 Å). These changes in the interatomic distances in the structures of **2** and **3** are qualitatively and quantitatively identical. The C(1)—C—O angle also changes only slightly in this series of compounds (**1**—**3**) and is equal to ~125, 123, and 123°, respectively. The geometries of

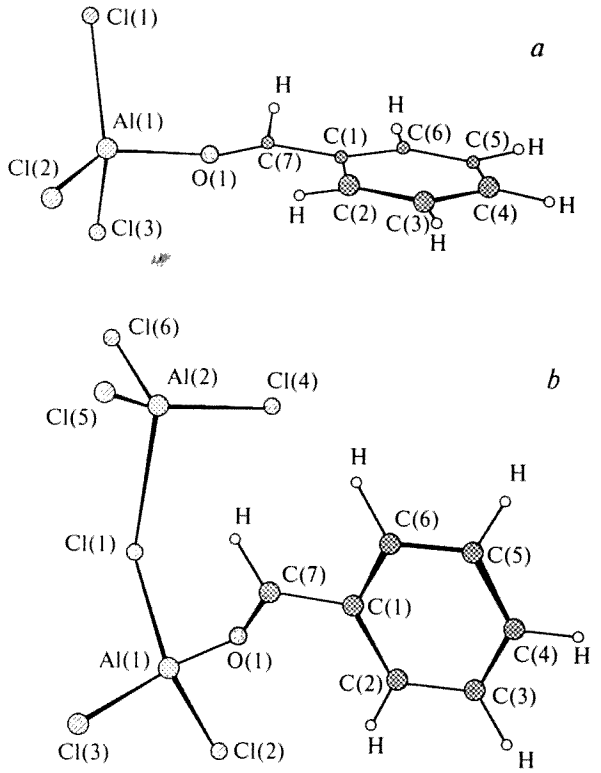


Fig. 1. Structure of the $PhCHO \cdot AlCl_3$ (*a*) and $PhCHO \cdot 2AlCl_3$ (*b*) complexes based on the results of the MNDO calculations.

both complexes optimized by the MNDO method correspond to the *E*-isomers. The coplanarity typical of the isolated benzaldehyde molecule is virtually retained when it is involved in complexes **2** и **3**: the angle between the C=O bond and the plane of the benzene ring is 6—7°, *i.e.*, the conditions favorable for the efficient conjugation between the carbonyl group, which is modified upon complex formation, and the aromatic system are essentially preserved. The Al(1) atoms in complexes **2** and **3** deviate also only slightly from the HCO plane; however, in compound **3**, the angle between this plane and the Al(1)ClAl(2) plane is ~60°. The bond angles at the Al(1) and Al(2) atoms are close to tetrahedral. The C—O—Al(1) angle in complexes **2** and **3** increases to 145 and 159°, respectively.

Complex formation is accompanied by a substantial electron density transfer from donor molecule **1** to the acceptor molecule. The total charges on $AlCl_3$ (−0.32) and Al_2Cl_6 (−0.35), like those on the atoms of the coordinated PhCHO fragment in complexes **2** and **3** that formed, are very similar. In particular, the charges on the corresponding carbon atoms of benzene rings in complexes **2** and **3** differ by no more than 0.02, which agrees well with the parameters of the ^{13}C NMR spectra of benzaldehyde and its 1 : 1 and 1 : 2 complexes with aluminum chloride.[4] On the whole, the results of calculations (see Fig. 1) confirm the spatial structures of the 1 : 2 complexes suggested previously.[4] Taking into account that the $Al(2)Cl_3$ fragment is substantially remote from the coordinated benzaldehyde molecule in complex **3** (the distances from the C(2) and C(6) atoms to Cl atoms are ~8 Å; the distance between C(CO) and Cl(6) is ~6.5 Å), two-center covalent (resonance) energy contributions can be ignored because they are negligibly small, and only purely ionic (Coulomb) components should be considered.[8,9] In particular, the two-center ionic components of the energy of interaction between the atoms of the $Al(2)Cl_3$ fragment and the carbonyl C atom ($E_{C-Al} \approx +1.5$, $E_{C-Cl(4)} \approx -0.8$, $E_{C-Cl(5)} \approx -0.7$, and $E_{C-Cl(6)} \approx -0.4$ eV) indicate that these fragments are as a whole prone to attraction ($E_{\Sigma} \approx -0.4$ eV).

Assuming that the Coulomb attraction between C(CO) and $Al(2)Cl_3$ is an important factor ensuring the occurrence of the 1 : 2 molecular compound, the fact that aliphatic ketones form only 1 : 1 complexes can also be explained: it is the aromatic or heteroaromatic (but not the alkyl) substituent at the carbonyl group that stabilizes the positive charge on the carbonyl C atom due to conjugation.

As follows from the experimental data,[2] the electric dipole moment increases sharply upon complex formation. The quantum-chemical calculations demonstrated (in agreement with the experimental data[2]) that the dipole moments of the 1 : 1 and 1 : 2 molecular compounds under consideration are rather similar: in none of the aromatic and heteroaromatic ketones studied previously[2] is the increase in the dipole moment in going from the 1 : 1 complex with $AlBr_3$ to the 1 : 2 adduct more than 0.6 D. All the experimental values of dipole moments[2] of the complexes are within the range of 9.2—11.0 D.

It is also worthy of note that the differences in the orbital energies of the lowest unoccupied and the highest occupied molecular orbitals ($\Delta E_{f\to v}$) for model systems **2** and **3**, which correlate with electronic excitation energies and, therefore, are often accepted as the measure of the reactivity,[10] differ only slightly. This agrees with the known data on the identical behavior of the 1 : 1 and 1 : 2 complexes of carbonyl compounds of the benzene, thiophene, and furan series in electrophilic substitution reactions.[11] Unlike the value of $\Delta E_{f\to v}$, the calculated ionization potential increases rather substantially as the degree of coordination of benzaldehyde increases, which is reasonably attributable to the direction of the resulting electron shifts (see Table 1).

The results of the calculations for the $AlCl_3$ and Al_2Cl_6 molecules (clearly, the values of $\Delta_f H$ and the geometric parameters as well as *IP* for $AlCl_3$ coincide with those determined by the same method and published previously[12]) are also given in Tables 1 and 2. We failed to determine the electronic structure of the optimized "half-cleaved" dimer $Cl_2Al—Cl—AlCl_3$ by the MNDO method because the corresponding local minimum was not observed on the potential energy surface. Note that the analogous $Br_2Al—Br—AlBr_3$ structure was found[13] by the related semiempirical AM1 method;

however, the calculated enthalpy of the reaction $2AlBr_3 \rightarrow Br_2Al{-}Br{-}AlBr_3$ was only -4.7 kcal mol^{-1} (for $2AlBr_3 \rightarrow Br_2Al(\overset{Br}{\underset{Br}{\diagup\diagdown}})AlBr_2$, it is -18.5 kcal mol^{-1}). Taking into account that the differences in the Al—Cl and Al—Br bond lengths in the Al_2Cl_6 and Al_2Br_6 molecules are in the range of 0.1—0.15 Å (the lengths of the terminal bonds are 2.06 and 2.21 Å; the lengths of the bridging bonds are 2.21 and 2.33 Å, respectively),[14] the geometric parameters of the $Br_2Al{-}Br{-}AlBr_3$ dimer calculated in Ref. 13 are rather close to those of the $Cl_2Al{-}Cl{-}AlCl_3$ fragment in complex **3**.

Based on the data given in Table 1, the enthalpies of reactions (1)—(4) ($\Delta_R H$) can be estimated. They are -25.6, -9.2, -20.3, and -14.5 kcal mol^{-1}, respectively.

$$PhCHO + AlCl_3 \rightarrow PhCHO \cdot AlCl_3 \quad (1)$$

$$PhCHO \cdot AlCl_3 + AlCl_3 \rightarrow PhCHO \cdot 2AlCl_3 \quad (2)$$

$$PhCHO + Al_2Cl_6 \rightarrow PhCHO \cdot 2AlCl_3 \quad (3)$$

$$AlCl_3 + AlCl_3 \rightarrow Al_2Cl_6 \quad (4)$$

The experimental data on the enthalpy of formation of complex **2** (taking into account the energy of dimerization of $AlCl_3$, it is -38.7 kcal mol^{-1}) are reported.[15,16] However, it is very difficult to compare the experimental value with that calculated for reaction (1) because calorimetric measurements were carried out for the reaction between solid aluminum chloride and a solution of liquid benzaldehyde **1** in chlorobenzene, which yielded insoluble, like $AlCl_3$, complex **2**, while in our calculations the effect of the polar solvent was ignored and, therefore, our results characterize the process in the gas phase (or in a non-polar solvent). To reduce the experimental heat to that in the gas phase, corrections for enthalpies of evaporation, sublimation, and solvation of all components of the reaction should be applied.[17]

To illustrate that the above-mentioned effects are difficult to take into account, it suffices to mention that in the fundamental monograph,[17] the thermodynamic characteristics for only seven nv complexes of aluminum chloride were given after a critical selection, whereas the characteristics for more than 80 complexes of aluminum bromide soluble in non-polar solvents were reported. A comparison of the data (though scarce) for the complexes of aluminum chloride and aluminum bromide containing the same donors demonstrates that the enthalpies of complex formation reduced to the gas phase are very similar for the two halides (Table 3). The same is true for the energies of dimerization of $AlCl_3$ and $AlBr_3$ (14.5 and 13.3 kcal mol^{-1}, respectively[18]).

The energy characteristics of the coordination bonds between heteroatoms and aluminum chloride and aluminum bromide are similar, as evidenced by the virtual identity of the ^{13}C NMR spectra of the complexes of carbonyl compounds of the benzene series with these two halides. Therefore, a comparison of the calculated values given above with the experimental data on aluminum bromide is rather justified. This comparison indicates that the values of $\Delta_R H$ calculated for reaction (1) and the enthalpy of formation of the $PhCHO \cdot AlBr_3$ complex in benzene (-36.7 kcal mol^{-1})[2] agree reasonably well. Similar or identical values (-37.8 kcal mol^{-1}) were obtained for the analogous complexes with acetophenone and benzophenone.[2] The enthalpy of complex formation of benzophenone with aluminum bromide, which is related to reaction (3), is -25.2 kcal mol^{-1}.[2]

Table 3. Enthalpies of formation ($-\Delta_R H$) of the complexes with aluminum chloride and aluminum bromide reduced to the gas phase

Donor	$-\Delta_R H$/kcal mol^{-1}	
	$AlCl_3$	$AlBr_3$
Et_2S	29.9	30.6
$(CH_2)_4S$	30.2	31.7
NH_3	41.0	41.0
C_5H_5N	45.7	45.3
4-EtC_5H_4N	46.0	47.4

Therefore, the quantum-chemical MNDO calculations of the model systems, on the one hand, reproduce reasonably well some physical and chemical properties of the complexes of carbonyl compounds with aluminum halides, which were determined experimentally, and on the other hand, rule out rather convincingly the occurrence of the 1 : 2 molecular compounds with a complete decomposition of the Al_2X_6 dimer. Heats of complex formation $\Delta_R H$ calculated with the use of the values of $\Delta_f H$ given in Table 1 are indicative of the preference of structure **3** containing a "half-cleaved" dimer as an acceptor.

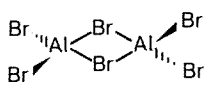
The structure under consideration agrees also with the experimental data, which we obtained for the low-frequency regions of the IR spectra of the complexes of benzophenone with $AlBr_3$. Previously,[5] the analysis of the shape of the C=O stretching band in the IR spectrum of the 1 : 2 complex of benzophenone with $AlBr_3$ suggested that the complex occurs as *syn—anti* and rotational isomers.[5] This agrees with the suggestions which were made[4] based on the analysis of the ^{13}C NMR spectra and which were supported by the results of quantum-chemical calculations performed in the present work. However, we failed to interpret the differences observed[5] in the low-frequency regions of the IR spectra of the complexes with different compositions (1 : 1 and 1 : 2), which does not allow us to suggest unambiguously the structures of these complexes based on the assignment of the Al—Br and Al—O stretching frequencies.

We did not seek to interpret completely the low-frequency regions of the spectra of the $Ph_2CO \cdot AlBr_3$ and $Ph_2CO \cdot 2AlBr_3$ complexes and only made the probable assignment of a number of Al—Br bands, which differ in intensity and position, and the bands which we observed in the spectrum of only one of the complexes (see Table 4).

Table 4. IR spectral characteristics of the complexes of benzophenone with aluminum bromide

ν/cm^{-1}		Assignment
$Ph_2CO \cdot AlBr_3$	$Ph_2CO \cdot 2AlBr_3$	
225 w, 250 w		$AlBr_3$
280 w	280 m	$Br—AlBr_2$
295 m	295 m	
	335 w	$Br—AlBr_3$ or $AlBr_3$
360 m	360 m	
375 m	380 m	
395	398 w	
430 s	430 s	
465 m	470 m	
505 w	490 m	$AlBr_3$

When analyzing the IR spectra, we used the published data[19] on the calculated frequencies of normal vibrations for the ordinary Al_2Br_6 dimer with two bridging Br atoms (**4**) and for the form with one bridge (**5**). The results of these calculations made it possible to interpret the Raman spectra of the complexes of a number of methylbenzenes with aluminum bromide reported previously.[20] It was demonstrated that in the complexes of di-, tri-, and tetramethylbenzenes of composition ArH : $AlBr_3$ = 1 : 2, aluminum bromide occurs as a dimer **5** (with one bridging Br atom), which is analogous to structure **3** considered above. When we interpreted the IR spectra of the complexes of benzophenone with aluminum bromide, the data[21,22] on the assignment of the bands of the vibrational spectra of the Al_2Br_6 and $AlBr_3$ molecules were also taken into account.



4

$Br_2Al—Br—AlBr_3$

5

In the low-frequency region of the IR spectrum of the $Ph_2CO \cdot 2AlBr_3$ complex, the medium intensity band occurs at 280 cm^{-1}, which, judging from the Raman spectra of the complexes of methylbenzenes with Al_2Br_6,[19,20] corresponds, apparently, to the vibrations of the Al—Br—Al bridge in the "half-cleaved" dimer **5**. An analogous low-intensity band occurs in the spectrum of the 1 : 1 complex and is absent in the spectrum of the Al_2Br_6 dimer.[21,22] The IR spectrum of the 1 : 1 complex, unlike that of the 1 : 2 complex, contains weak bands at 225 and 250 cm^{-1}. Based on the data[22] on the monomeric $AlBr_3$ molecule, these bands can be assigned to vibrations of the $AlBr_3$ fragment in the 1 : 1 complex. The IR spectrum of the 1 : 2 complex shows a weak band at 335 cm^{-1} (in the case of the 1 : 1 adduct, this band is absent), which can be assigned to stretching vibrations of the Al—Br bond of the bridging (*cf.* Ref. 21) or terminal (*cf.* Refs. 19 and 20) fragment of dimer **5**. Finally, the IR spectrum of the 1 : 2 complex shows also a band at 490 cm^{-1}, and in the spectrum of the 1 : 1 complex, the corresponding low-intensity band occurs at 505 cm^{-1}. Taking into account the results of calculations[19] and the assignments[21,22] made for the molecule of dimer **4**, these bands can be attributed to asymmetric stretching vibrations of the Al—Br bonds in the $AlBr_3$ groups of the complexes with the dimeric (type **5**) and monomeric fragments, respectively. The assignments of the above-mentioned bands at 490 and 505 cm^{-1} to the Al—O stretching vibrations by analogy with the data[23,24] on Al β-diketonates is less reasonable. Judging from the assignments reported in Refs. 17 and 25 for the related $AlBr_3$ complexes, most likely the 550—580 cm^{-1} range corresponds to the Al—O vibrations, which in our case overlaps with absorption bands of polyethylene.

Therefore, the IR spectral data agree on the whole with the interpretation of the Raman spectra of the complexes of methylbenzenes with aluminum bromide,[19] in particular, with the suggestion that the bridging fragment of **5** occurs in the 1 : 2 complex. All characteristic features[19] of the spectra of the complexes of methylbenzenes with Al_2Br_6 are also observed in the IR spectrum of the 1 : 2 molecular compound of benzophenone with $AlBr_3$, which (in agreement with the results of quantum-chemical calculations) is indicative of the existence of the $Br_2Al—Br—AlBr_3$ fragment in this compound.

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