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On the structure of benzene halogen complexes A matrix isolation study

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The infra-red spectra of 1 : 1 complexes between benzene and chlorine, bromine, and iodine chloride have been studied, with the complexes isolated in a nitrogen matrix at 20 K. The results are interpreted as evidence for an oblique complex structure, with the halogen molecule interacting mainly with one of the C=C bonds.

1. INTRODUCTION

In his earliest papers on charge transfer complexes, Mulliken [1, 2] discussed possible structures of benzene-halogen complexes. Using an argument based on considerations of orbital symmetry and maximum Coulomb attraction between donor and acceptor ions, he concluded that the complex probably had an equilibrium structure with the halogen bond parallel to the benzene plane. A few years later, Collin and d'Or [3, 4] found that the stretching vibration of chlorine become infra-red active in benzene solution. They interpreted this as evidence against this equilibrium structure. Mulliken suggested an oblique structure [5] for the benzene-chlorine complex, for instance with one chlorine atom above one C-C bond.

However, as was pointed out by Ferguson and Matsen [6, 7], the transition dipole of the chlorine stretching vibration may very well be orthogonal to the chlorine bond and thus the basis for the argument against the original structure is not valid.

Ferguson [8-10] argued that the complexes had an axial structure from the observation that the infra-red bands at 850 and 992 cm^{-1} were appreciably enhanced in intensity in solutions of bromine and iodine in benzene while the remaining bands seemed unaffected.

Hassel and co-workers studied the solid benzene-bromine [11] and benzene-chlorine [12] complexes by X-ray crystallography. They found that the crystals consisted of chains of alternating halogen and benzene molecules, thus lending further support to the axial structure.

Person *et al.* [13] studied the infra-red spectra of polycrystalline bromine benzene mixtures. They found that the bromine-bromine stretching vibration was infra-red active, though it should be inactive in the complex structure found by Hassel and Strømme. They concluded that either they studied a different crystal structure or else the structure of Hassel and Strømme is incorrect. They did not question the axial arrangement of the halogen relative to the benzene,

in fact they interpreted their data as support for a C_{3v} site symmetry for benzene, which rules out a resting complex structure.

However, Mulliken has repeatedly stressed that the crystalline complexes should be considered as $n : n$ complexes [14] and therefore no really safe conclusions about the structure of isolated 1 : 1 complexes may be obtained from studies of crystalline complexes.

This investigation has been undertaken since it was felt that the matrix isolation technique might offer a unique way of obtaining sufficient complex concentration without too large a disturbing effect from the free components, because of the very sharp infra-red absorptions of matrix isolated molecules [15–17]. Ultra-violet spectra of matrix isolated benzene iodine complexes have previously been reported in a number of different matrices [17b].

2. EXPERIMENTAL

The cryostat used was described earlier [18]. The temperature of the caesium iodide window was kept at 20 ± 0.1 K in all experiments. The deposition set-up allows two separate gas mixtures to be introduced into the cryostat simultaneously. Each gas flow can be kept constant to better than ± 0.3 per cent of any desired flow by two servo regulated metering valves (a detailed description will be published later [19]). In all experiments the deposition rate was kept at 1.5 ± 0.005 mmol/h (in total).

Benzene and halogen were mixed with nitrogen in two separate volumes. Pressures of benzene and halogen were measured with a Rosemount Eng. Co. capacitive pressure transducer (model 831A, 0–0.2 psia). Nitrogen pressures were measured with a bellows manometer (NAF 31880, 0–240 torr) calibrated against a mercury manometer. Approximately 1 mmol of pure nitrogen was deposited before and after the deposition of the gas mixture. In all experiments approximately 45 mmol of gas mixture was deposited.

Nitrogen (L'Air Liquide A-56, 99.9996 per cent pure) was passed through a glass spiral immersed in liquid nitrogen and used without further purification. Benzene (Fisher B 245) was purified by fractional crystallization and distillation on a vacuum line. Chlorine (Matheson, 99.5 per cent pure) was passed over activated charcoal and molecular sieves and then through concentrated sulphuric acid. It was degassed and distilled from -78°C to -196°C . Bromine was distilled in vacuum from -78°C to -196°C . Iodine chloride (BDH) was purified by fractional crystallization, degassed and distilled on a vacuum line.

All infra-red spectra were recorded on a Perkin-Elmer 180 instrument which was calibrated with standard gases [20]. Note that the figures were reproduced directly from spectra and were not corrected.

3. RESULTS AND ASSIGNMENTS

3.1. Benzene

For benzene alone in a nitrogen matrix, a large number of absorptions were observed. These could be classified on the basis of their behaviour when the matrix was warmed to 30.5 K to allow benzene to diffuse. In general, one set of sharp absorptions decreased, or in the case of some weak absorption peaks, disappeared. The second set of absorption peaks increased upon diffusion.

The peaks in this set were, in general, broader than those of the first set. Both sets of absorptions were close to gas phase values of benzene fundamentals or

Assignment	Benzene monomer matrix (cm ⁻¹)	Calculated matrix (cm ⁻¹)	Gas (cm ⁻¹)
ν_1			3073
ν_2		992 (f)	993
ν_3		1346	1350
ν_4	678.6	678.6	673
ν_5			3057
ν_6	1009.1 (e)	1009.1	1010
ν_7		993	990
ν_8	698.8 (e)	705	707
ν_9		1301	1309
ν_{10}		1147	1146
ν_{11}		849	846
ν_{12}			3064
ν_{13}	1482.9	1482.9	1482
ν_{14}	1039.8	1039.8	1037
	1038.1		
ν_{15}			3056
ν_{16} (a)	1589.1 (e)	1589.1	1590
ν_{17}	1180.0 (e)	1177	1178
ν_{18}		611	606
ν_{19}		968	967
ν_{20}		399	398
$\nu_2 + \nu_{18}$ (a)	1607.4 (e)	1607.4	1610
ν_{13} ¹³ C	1475.3		
$\nu_{11} + \nu_{20}$	1248.2	1248	1242
$\nu_7 + \nu_{20}$	1392.6	1392	1388
	1391.6		
$\nu_4 + \nu_{11}$	1527.6	1528	1522
$\nu_6 + \nu_{18}$	1619.8	1620	1622
$\nu_2 + \nu_4$			1667
$\nu_8 + \nu_{19}$	1671.1		1673
$\nu_8 + \nu_6$	1713.8	1714	1716
$\nu_{10} + \nu_{18}$	1757.9	1758	1755
$\nu_{11} + \nu_{19}$	1816.9	1817	1811
$\nu_7 + \nu_{19}$	1961.0	1961	1958
$\nu_{14} + \nu_{17}$	2217	2217	2214
$\nu_6 + \nu_{16}$ (b)	2598.6	2598	2600
$\nu_2 + \nu_{18} + \nu_6$ (b)	2617.0	2617	2620
	2820.5		
$\nu_3 + \nu_{13}$	2828.7	2829	2827
	2855.1		2853
$\nu_9 + \nu_{16}$ (c)	2889.4	2890	2899
$\nu_2 + \nu_{18} + \nu_9$ (c)	2908.4	2908	2919
ν_{12} (d)	3044		3047
$\nu_{13} + \nu_2 + \nu_{18}$ (d)	3077		3083
$\nu_{13} + \nu_{16}$ (d)	3099		3100

(a) Fermi resonance pair. (b) Fermi resonance pair. (c) Fermi resonance pair. (d) Fermi resonance trio. (e) Very weak, almost disappears upon diffusion. (f) Using the assignment $\nu_2 + \nu_4 = 1671.1$.

Table 1. Observed benzene absorptions in a nitrogen matrix at 20 K, compared with results from a combination band analysis and gas phase data [21].

combination bands. The first set was assigned to monomeric benzene, and the second set to benzene aggregates. In most cases the assignments within each set presented no particular difficulty, each absorption could be assigned to a benzene fundamental or combination band directly from comparison with the gas phase data [21]. The only doubtful case is the assignment of the peak at 1671 cm^{-1} , where two very reasonable possibilities exist; it can be assigned to $\nu_2 + \nu_4$ or to $\nu_8 + \nu_{19}$. The fundamental frequencies of benzene are numbered as by Herzberg [22] instead of the more common numbering by Wilson [23], since we consider this numbering more in line with other cases.

The first possibility leads to a value for ν_2 of matrix isolated benzene as 992 cm^{-1} , a very reasonable figure. For the other assignment we calculate $\nu_8 + \nu_{19} = 1673\text{ cm}^{-1}$, from the value of ν_8 and ν_{19} given in table 1.

No attempt was made to study the concentration dependency of the benzene aggregate absorptions in order to determine their size. The observed absorptions and their assignments are given in table 1. This table also gives a comparison between the observed combination bands in the matrix and in the gas phase [21]. From the observed combination frequencies, values were calculated for some of the inactive fundamentals of benzene. Table 1 also gives a comparison between the calculated and observed fundamentals of benzene in the gas phase [21] and in the nitrogen matrix. The combination bands calculated from the fundamentals are also given.

Considering the observations of Brodersen and Langseth [21] of the small anharmonicities of benzene, we expect the calculated fundamentals to be close to the correct values.

3.2. Benzene-bromine

306 region. In the spectra of the benzene-bromine-containing matrices, there appears a peak with two barely visible shoulders at 306 cm^{-1} . Since it varies with benzene and bromine concentration roughly in the way expected for a 1:1 benzene-bromine complex (table 2), it seems safe to assign it to the Br-Br stretching vibration of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

607 region. The 607 region of benzene has a weak absorption peak. It is assigned to benzene aggregates because of its diffusion behaviour. The benzene-bromine spectra have a second peak. As is seen from table 2, this second peak varies with benzene and bromine concentrations, approximately as expected for a 1:1 complex. Unfortunately, the absorption is very low and does not permit any safe conclusions from the concentration behaviour alone. The absorbance of the benzene-bromine matrix is higher than that of the benzene matrix, in spite of the fact that the benzene concentrations and the amounts deposited were very nearly equal in the two cases. Since the rates of deposition were the same in both cases (the automatic flow regulation referred to above makes possible very even and reproducible rates of deposition), we expect a lower benzene aggregate concentration in the benzene bromine matrix. A comparison of the 850 cm^{-1} (figure 2), 1820 cm^{-1} and 1960 cm^{-1} (figure 1) regions of the benzene bromine experiment considered with the benzene experiment before and after diffusion, indicates that this expectation is fulfilled. We therefore feel justified to assign the absorption at 606.7 cm^{-1} to ν_{18} of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

680 region. Monomeric benzene in a nitrogen matrix has its strongest absorption at 678.6 cm^{-1} . In the benzene aggregates, this absorption is shifted

to higher wave numbers, and falls in the interval between 680 and 685 cm^{-1} . For the bromine-benzene-containing matrices, this absorption has a very strong satellite at 687.7 cm^{-1} . The overlap with the benzene absorption makes it

ν^\dagger (cm^{-1})	A	Absorbance B	C	Remarks
304.6	0.134		0.047	Shoulder
306.3	0.166	0.105	0.073	
307.9	0.102	0.075	0.057	Shoulder
606.7	0.019	0.012	0.016	
702.4	0.104	0.050	0.056	
858.7	0.080	0.044	0.044	Shoulder
860.5	0.145	0.086	0.077	
972.8	0.048	0.026	0.030	
974	0.033	0.015	0.020	Shoulder
990.8	0.156	0.094	0.086	
1009.1	0.022	0.010	0.015	
1011.6	0.022	0.005	0.015	
1021.8	0.068	0.073	0.040	
1025.7	0.028	0.028	0.015	
1036.9	0.666	0.325	0.570	
1038.1	0.735	0.398	0.733	
1039.8	0.596	0.340	0.611	
1151.0	0.025	0.012	0.017	
1178.6	0.061	0.030	0.050	
1180.0	0.047	0.025	0.040	
1312.1	0.060	0.041	0.035	
1527.6	0.118	0.079	0.149	
1538.9	0.035	0.013	0.018	
1546.4	0.029			
1585.8	0.066	0.035	0.036	
1589.1	0.036	0.012	0.040	
1604.3	0.065	0.030	0.043	
1607.4	0.025	0.010	0.027	
1618.6	0.029	0.015	0.022	
1619.8	0.040	0.022	0.033	
1816.9	0.342	0.213	0.427	
1826.0	0.100	0.050	0.075	
1830.7	0.072	0.041	0.041	
1961.0	0.204	0.132	0.265	
1969.9	0.090	0.045	0.066	
3044	1.257	0.717	1.305	
3077	0.382	0.215	0.458	
3099	0.851	0.478	0.905	

\dagger A number of benzene absorptions, which were irrelevant for the arguments in this paper, were left out, in order to make the table easier to read. Experiment concentrations :

	$\text{N}_2 : \text{C}_6\text{H}_6$	$\text{N}_2 : \text{Br}_2$	mmoles N_2 deposited
A	92	79	48
B	180	79	47
C	93	158	42.5

Table 2. Results of a concentration dependency study for benzene, bromine absorption.

impossible to study its concentration dependency. However, its high absorbance and closeness to ν_4 of free benzene makes it necessary to assign the satellite at 687.7 cm^{-1} to ν_4 of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

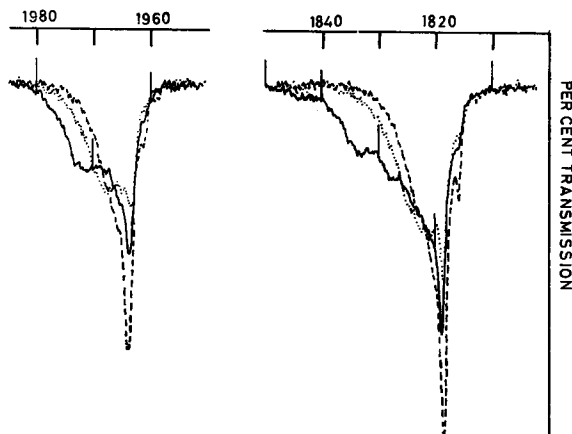


Figure 1. The $\nu_{11} + \nu_{19}$ and $\nu_7 + \nu_{19}$ regions of C_6H_6 (---: immediately after deposition), (····: after 5 min at 30.5 K) (N_2 : C_6H_6 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ (—) (N_2 : C_6H_6 92, N_2 : Br_2 79, mmoles deposited 48).

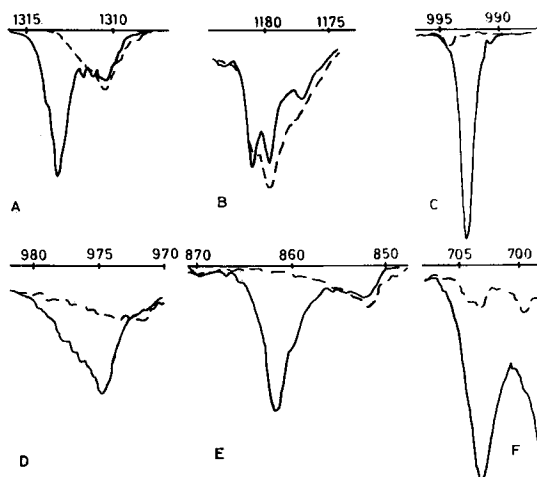


Figure 2. (A) The ν_9 (B_{2u}) region of C_6H_6 (---) (N_2 : C_6H_6 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ (—) (N_2 : C_6H_6 93, N_2 : Br_2 158, mmoles deposited 42.5). (Per cent transmission.) (B) The ν_{17} (E_{2g}) region of C_6H_6 (—) (N_2 : C_6H_6 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ (---) (N_2 : C_6H_6 92, N_2 : Br_2 79, mmoles deposited 48). (C) The ν_2 (A_{1g}) region of C_6H_6 : (---) (N_2 : C_6H_6 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ (—) (N_2 : C_6H_6 93, N_2 : Br_2 158, mmoles deposited 42.5). (Per cent transmission.) (D) The ν_{19} (E_{2u}) region of C_6H_6 (---) (N_2 : C_6H_6 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ (—) (N_2 : C_6H_6 92, N_2 : Br_2 79, mmoles deposited 48). (E) The ν_{11} (E_{1g}) region of C_6H_6 (---) (N_2 : C_6H_6 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ (—) (N_2 : C_6H_6 93, N_2 : Br_2 158, mmoles deposited 42.5). (Per cent transmission.) (F) The ν_8 (B_{2g}) region of C_6H_6 (---) (N_2 : C_6H_6 93, mmoles deposited 48) and (—) $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ (N_2 : C_6H_6 92, N_2 : Br_2 79, mmoles deposited 48).

700 region. Benzene in a nitrogen matrix has two very weak absorptions in this region, one at 698.8 cm^{-1} , which disappears upon diffusion, and one at 702.9 cm^{-1} , which increases. As is seen from figure 2 F the bromine-containing matrices have an absorption at 702.4 cm^{-1} , which is approximately ten times more intense than the 702.9 peak of benzene. Its absorbance varies with benzene and bromine concentration as expected for a 1 : 1 complex, as is seen from table 2. We therefore feel confident that it should be assigned to ν_8 of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$. Spectra of crystalline benzene show a weak absorption at 707 cm^{-1} , which has been assigned to crystal field splitting of ν_4 [24] or a combination with lattice modes [25]. These interpretations seem impossible in this case, considering that other regions of the spectrum of benzene-bromine or benzene-containing matrices show no signs of the complicated crystal field splitting of benzene.

860 region. Benzene in a nitrogen matrix shows a weak absorption at *ca.* $851\text{--}853\text{ cm}^{-1}$, which increases upon diffusion. When bromine is also present in the matrix, a relatively strong peak at 860.5 cm^{-1} , with a weak shoulder at 858.7 cm^{-1} , appears (figure 2 E). Its concentration dependency (table 2) and its closeness to ν_{11} of free benzene makes us assign it to ν_{11} of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

980 region. In this region the benzene-bromine-containing matrices show two absorptions which are not present with benzene alone, see figures 2 C and 2 D. Both peaks, and the shoulder of the low wave number peak, vary with concentrations, as expected for a 1 : 1 complex. There are four benzene fundamentals which might contribute in this region, ν_2 (A_{1g} , 992 cm^{-1}), ν_6 (B_{1u} , 1009 cm^{-1}), ν_7 (B_{2g} , 993 cm^{-1}) and ν_{19} (E_{2u} , 967 cm^{-1}). Of these, ν_6 seems to be too far from the observed peaks to be a real possibility. Since ν_{19} is degenerate in free benzene and may split as a result of the complex formation, we tentatively assign the peak and shoulder at 972.8 and 974 cm^{-1} , respectively, to ν_{19} of the complex. This assignment implies a small complex shift, while the alternative assignments ν_2 and $\nu_7 = 972.8\text{ cm}^{-1}$ imply large shifts and, in the case of ν_7 , in an unexpected direction. The remaining absorption is assigned to ν_2 of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$, since ν_7 is expected to shift towards higher wave numbers in the same way as the other CH out-of-plane fundamentals (ν_4 : 9 cm^{-1} , ν_{11} : 12 cm^{-1} (one component only), ν_{19} : 5 cm^{-1}). The assignment of 990.8 to ν_7 would imply a small decrease of ν_7 upon complex formation. It must be noted that the assignments in this region are only tentative (see, however, below).

1000–1030 region. In this region the benzene-bromine-containing matrices have four absorptions. The first one, at 1009.1 cm^{-1} , is present with benzene alone, is very weak and disappears upon diffusion. It is therefore assigned to monomeric benzene. There is another small peak at 1011.6 cm^{-1} , which might have been ν_6 of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$. However, its concentration dependence (table 2) indicates that it is due to a species with at least two benzene and one bromine molecule. Finally there are two absorptions at 1021.8 cm^{-1} and 1025.7 cm^{-1} , which seem to have a common origin. Their concentration dependency is similar (table 2) and both disappear when the temperature is increased to allow benzene to diffuse in the matrix. A similar pair of absorptions was observed with chlorine at 1022.5 cm^{-1} and 1026.4 cm^{-1} . Since there are no other absorptions with a similar concentration dependency, we are unable to say anything about the absorbing species except that it seems to contain more than one halogen molecule.

1040 region. Assignments of the complex absorptions are difficult, since the allowed benzene fundamental (ν_{14} , E_{1u}) of monomeric and polymeric benzene dominates the observed absorption. However, the maximum at 1036.9 cm^{-1} seems to have a complex origin. Its concentration dependency is difficult to assess, but we believe that its strength indicates that it should be assigned to $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

1150 region. Benzene-containing matrices have a very weak and broad absorption around 1150 cm^{-1} , which gets a high frequency satellite when bromine is added. The concentration dependency of this satellite is difficult to measure. However, it seems to be consistent with a 1 : 1 complex (table 2) and we therefore assign the peak at 1151.0 cm^{-1} to ν_{10} of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

1180 region. Both benzene and benzene-bromine-containing matrices absorb in this region (see figure 2 B). The rather small difference in wave numbers between the maxima of the strongest benzene aggregate absorption and the strongest peak of the benzene-bromine matrices seems to make assignments difficult. As was argued above (see discussion of the 607 region), the concentration of benzene aggregates should be small in the benzene-bromine-containing matrices, and we therefore think it is justified to assign the maximum at 1178.5 cm^{-1} to some benzene-bromine complex. Its concentration dependency is uncertain because of the overlap with the benzene absorption, but since it does not contradict a 1 : 1 complex origin of the 1178.5 peak, we tentatively assign this maximum to ν_{17} of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

1310 region. As is shown in figure 2 A the benzene-bromine-containing matrices have a sharp absorption at 1312.1 cm^{-1} which is not present for benzene alone. Its concentration dependence (table 2) shows that it is caused by a 1 : 1 complex between benzene and bromine, and we therefore confidently assign it to ν_9 of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

1480 region. Since the benzene ν_{13} (E_{1u}) is infra-red active and strong, it is almost impossible to obtain any detailed information about the ν_{13} fundamental of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$. For the bromine-containing matrices, the ν_{13} peak broadens on the low wave number side, and as the benzene concentration is lowered, a satellite becomes visible at 1480.6 cm^{-1} . Its high intensity makes it likely that it should be assigned to $\text{C}_6\text{H}_6 \cdot \text{Br}_2$. When bromine is present in the matrix the ^{13}C satellite at 1475.3 get a shoulder at 1474.5 cm^{-1} . It also gets a broad absorption on the low frequency side which extends *ca.* $1.5\text{--}2\text{ cm}^{-1}$ from the shoulder. We believe that the shoulder should be assigned to the ν_{13} fundamental of a ^{13}C complex. Note that the ^{13}C satellite of benzene is one of the two components into which the ν_{13} fundamental is split upon ^{13}C substitution. The other component is shifted only slightly from ν_{13} of $^{12}\text{C}_6\text{H}_6$. There may be several isomeric ^{13}C complexes, depending on the structure of the complex. We believe, however, that the isomer shifts are small and that both components of the ^{13}C satellite shift as the corresponding ^{12}C peaks, when the complex is formed.

We are thus led to believe that the ν_{13} fundamental of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ has a second component at 1482.1 cm^{-1} .

1600 region. In this region benzene in a nitrogen matrix shows two weak absorptions at 1589.1 cm^{-1} and 1607.4 cm^{-1} . These absorptions were assigned above the Raman-active Fermi doublet (ν_{16} , $\nu_2 + \nu_{18}$, E_{2g}) of monomeric benzene. The corresponding pair of the benzene aggregates is at 1588.6 and 1604.3 cm^{-1} .

The bromine-containing matrices showed, in addition to the benzene monomer pair, another pair at 1585.8 and 1604.3 cm^{-1} . The concentration dependence of this pair is consistent with a 1 : 1 complex origin and, as was discussed, the benzene aggregate concentration should be low, we assign the pair of absorptions at 1585.8 and 1604.3 cm^{-1} to the Fermi doublet (ν_{16} , $\nu_2 + \nu_{18}$) of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

Combination band regions. The bromine-containing matrices have in addition to the benzene combination bands a few weak satellites to the strongest benzene combinations. Their concentration dependence indicates a 1 : 1 complex origin and we therefore have assigned them accordingly. The combination of fundamentals ν_4 and ν_{11} of benzene at 1527.6 cm^{-1} gets two satellites at 1538.9 and 1546.4 cm^{-1} . The latter is close to the value calculated from the observed ν_4 and ν_{11} of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$, 1548.2 cm^{-1} . If we, for the moment, assume that one component of ν_{11} is very weak, and therefore not observed, but contributes to the combination band absorption, we calculate for this component of ν_{11} of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$ a value of 851 cm^{-1} . There may well be a weak complex absorption at 851 without being noticed, since the benzene aggregate absorption is fairly strong here. The combination $\nu_{11} + \nu_{19}$ of benzene at 1816.9 cm^{-1} gets two satellites at 1826.0 and 1830.7 cm^{-1} (see figure 1).

If we combine the observed component of ν_{11} with the strong component of the band assigned tentatively above to ν_{19} , we get 1833.3 cm^{-1} , i.e. reasonably close to 1830.7. The combination of the weak component of ν_{19} and the calculated component of ν_{11} gives 1825 cm^{-1} , close to the second satellite. The combination band $\nu_7 + \nu_{19}$ of benzene at 1961.0 cm^{-1} gets a satellite at 1969.9 cm^{-1} when bromine is present in the matrix (see figure 1). From the previously assigned values of ν_{19} we calculate ν_7 as 997 or 996 cm^{-1} . The above considerations are of a rather tentative nature, in particular the assumption of the

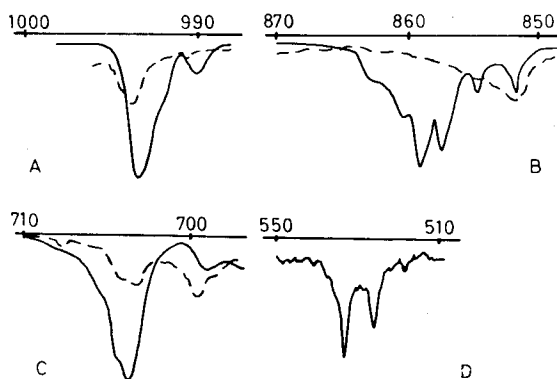


Figure 3. (A) The ν_2 (A_{1g}) region of C_6H_6 (---) (N_2 : C_6H_6 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{Cl}_2$ (—) (N_2 : C_6H_6 96, N_2 : Cl_2 51; mmoles deposited 35). (Per cent transmission.) (B) The ν_{11} (E_{1g}) region of C_6H_6 (---) (N_2 : C_6H_6 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{Cl}_2$ (—) (N_2 : C_6H_6 96, N_2 : Cl_2 51, mmoles deposited 35). (Per cent transmission.) (C) The ν_8 (B_{2g}) region of C_6H_6 (---) (N_2 : C_6H_6 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{Cl}_2$ (—) (N_2 : C_6H_6 96, N_2 : Cl_2 51, mmoles deposited 35). (Per cent transmission.) (D) The Cl-Cl stretching region of $\text{C}_6\text{H}_6 \cdot \text{Cl}_2$ (N_2 : C_6H_6 96, N_2 : Cl_2 51, mmoles deposited 35). (Per cent transmission.)

existence of a second component of ν_{11} at 851 cm^{-1} , disregarding the shoulder at 858.7 cm^{-1} . It must be noted, however, that different assignments of the 980 region would make it more difficult to assign the combination bands of the complex.

The combination $\nu_6 + \nu_{18}$ of the complex gives $\nu_6(\text{C}_6\text{H}_6 \cdot \text{Br}_2) = 1012\text{ cm}^{-1}$, i.e. exactly at the place where a weak absorption is found. This absorption had to be assigned to a ternary (or higher) complex. As explained above, however, it may perhaps hide the ν_6 fundamental of $\text{C}_6\text{H}_6 \cdot \text{Br}_2$.

Benzene-chlorine. No systematic studies of the concentration dependency of the spectra of benzene-chlorine-containing matrices were made. The spectra obtained were very similar to those of the benzene bromine case, and assigned on the basis of comparisons between bromine and chlorine. Figures 3 A, 3 C and 3 B give the results for the ν_2 , ν_8 and ν_{11} regions and should be compared to figures 2 C, 2 F and 2 E which illustrates the corresponding bromine spectra. Also in this case the halogen stretching fundamental became active. It is easily identified from its isotope splitting, as is seen from figure 3 D.

Benzene-iodine chloride. Since we feel that it is of interest to compare spectra of the benzene-bromine complex with results from benzene-iodine chloride; we include the results of a preliminary investigation of the benzene-iodine chloride complex in this paper. As is seen from a comparison between figures 4 C and 2 F (ν_8), 4 B and 2 E (ν_{11}) and of figures 4 A and 2 D (ν_{19}), the benzene-iodine chloride spectra are very similar to the corresponding benzene-bromine spectra. Figure 4 D shows the spectrum of the iodine chloride stretching region, compared with spectra of iodine chloride of similar concentration.

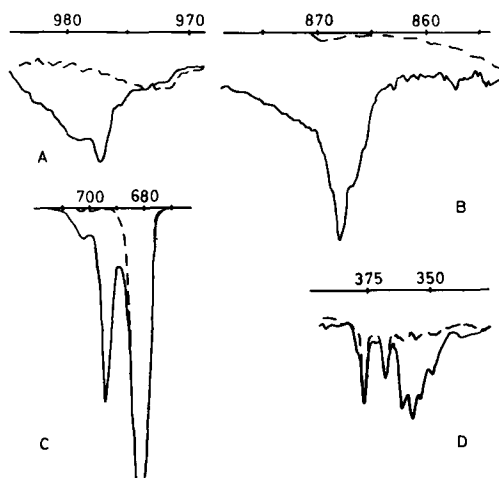


Figure 4. (A) The ν_{19} (E_{2u}) region of C_6H_6 (---) ($\text{N}_2 : \text{C}_6\text{H}_6$ 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{ICl}$ (—) ($\text{N}_2 : \text{C}_6\text{H}_6$ 92, $\text{N}_2 : \text{ICl}$ 93, mmoles deposited 45). (B) The ν_{11} (E_{1g}) region of $\text{C}_6\text{H}_6 \cdot \text{ICl}$ ($\text{N}_2 : \text{C}_6\text{H}_6$ 92, $\text{N}_2 : \text{ICl}$ 93, mmoles deposited 45). (C) The ν_4 (A_{2u}) and ν_8 (B_{2g}) regions of C_6H_6 (---) ($\text{N}_2 : \text{C}_6\text{H}_6$ 93, mmoles deposited 48) and $\text{C}_6\text{H}_6 \cdot \text{ICl}$ (—) ($\text{N}_2 : \text{C}_6\text{H}_6$ 92, $\text{N}_2 : \text{ICl}$ 93, mmoles deposited 45). (D) The I-Cl stretching region of $\text{C}_6\text{H}_6 \cdot \text{ICl}$ (—) ($\text{N}_2 : \text{C}_6\text{H}_6$ 92, $\text{N}_2 : \text{ICl}$ 93, mmoles deposited 45) and ICl (---) ($\text{N}_2 : \text{ICl}$ 94, mmoles deposited 31).

As is seen from the figure, the two absorptions at 376.3 and 367.8 cm^{-1} should be assigned to I^{35}Cl and I^{37}Cl , respectively. It is also seen from the figure that no significant absorptions which could be assigned to ICl aggregates were present initially in the ICl experiments. Such aggregates were formed only as a result of diffusion. Since the ICl concentrations were similar in the two experiments, and the rates of deposition identical, it seems unreasonable to assign any of the peaks of the benzene ICl experiment to ICl aggregates. We therefore believe that all four rather strong peaks in the 362–349 interval have to be assigned to benzene complexes. It should be noted that the four peaks must be assigned to two isotopic pairs (361.2, 353.5) and (356.6, 349.3), each with the intensity ratio 3 : 1. When the isotope splitting is taken into consideration the absorbance of the two pairs is seen from the figure to be roughly equal and we therefore have to assign both to 1 : 1 complexes between benzene and iodine chloride.

Assignment	Benzene	(Benzene) _n	Benzene-Cl ₂	Benzene-Br ₂	Benzene-ICl
ν_2		991.8	991.5	990.8	988.7
ν_4	678.6	680–685	688	687.7	693.1
ν_6	1009.1 (b)	1011.7			
ν_8	698.8 (b)	702.9	703	702.4	701.3
ν_9		1309.2	1311	1312.1	1314
ν_{10}		1151		1151.0	1151
		1148.3			
ν_{11}		852.3	858.0	860.5	866.6
		851	856.3 (c)	858.7 (c)	865.4 (c)
ν_{13}	1482.9	1481		1482.1	1479.5
				1480.6	1478
$\nu_{13}^{13}\text{C}$	1475.3	1474		1474.5	
ν_{14}	1039.8	1038.1			1036.3
	1038.1	1037.4	1038	1036.9	1034.8
ν_{16} (a)	1607.4 (b)	1604.3		1604.3	1604.7
$\nu_2 + \nu_{18}$ (a)	1589.1 (b)	1588.6	1587.6	1585.8	
ν_{17}	1180.0 (b)	1179.1	1178	1178.5	1178.8
		1175.9			
ν_{18}		607		606.7	606.1
ν_{19}		971	974	972.8	975.1
				974 (c)	977 (c)
ν_{XY}			532 (d)	307.9 (c)	361.2
			525	306.1 (e)	353.5
			517.5	304.7 (c)	356.6
$\nu_4 + \nu_{11}$	1527.6			1538.9	349.3
				1546.4	
$\nu_{11} + \nu_{19}$	1816.9		1827.4	1830.7	1838.0 \pm 5
			1824	1826	
$\nu_7 + \nu_{19}$	1961.0		1967	1969.9	1972
$\nu_6 + \nu_{18}$	1619.8			1618.6	

(a) Fermi resonance pair. (b) Very weak, almost disappears upon diffusion. (c) Shoulder. (d) Gas phase 556.9 cm^{-1} (ref. [27]). (e) Gas phase 321.11 cm^{-1} (ref. [27]).

Table 3. Observed fundamental vibrations and combinations bands for some benzene complexes (cm^{-1}).

4. DISCUSSION

From table 3 it is seen that most benzene fundamentals become active upon complex formation. Since the concentration dependence studies clearly showed that the complex absorptions were caused by a 1 : 1 complex, two explanations for the infra-red activity have to be considered. The benzene complex fundamentals may be perturbed by the nitrogen matrix in some unsymmetric manner, and therefore become infra-red active, or the symmetry of the complex may be sufficiently low to make the normal selection rules of benzene break down almost completely.

The sharpness of the complex absorptions rules out matrix perturbations as an explanation, and we therefore have to consider the symmetry of the complex.

For the axial complex structure, we expect only $\nu_2(A_{1g})$ and $\nu_{11}(E_{1g})$ to become active. However, both the resting and the oblique models have sufficiently low symmetry to make almost all fundamentals appear. The great similarity between the chlorine, bromine and iodine chloride complex spectra indicates that these complexes have very similar structures. For the iodine chloride complex there appear to exist two isomeric 1 : 1 complexes, as discussed above. Indeed, for the oblique structure, we do expect two isomeric forms of the complex. Since the temperature of the window is very low, we do not expect these two isomers to be able to rearrange into each other once formed. Therefore a 1 : 1 ratio of the two isomeric forms is expected. Thus the oblique model, in contrast to the resting model, gives a very reasonable explanation for the appearance of the ICl stretching region of the iodine chloride complex. To summarize the argument so far, we believe that our data strongly suggest an oblique complex structure for the 1 : 1 chlorine, bromine and iodine chloride complexes with benzene in a nitrogen matrix. Of course, our data cannot show whether this oblique structure is a result of interactions between the complex and the nitrogen matrix. While such an interaction is possible in principle, we believe it rather unlikely, considering for instance the very small gas to matrix shifts of the benzene fundamentals (see table 1). Accepting the oblique complex structure, we expect a plane of symmetry to remain. This plane may pass through a pair of carbon atoms (para to each other) or through a pair of C=C bonds. In both cases the benzene fundamentals may be classified as symmetric (A') or antisymmetric (A'') with respect to the plane of symmetry. Generally, we expect the A' fundamentals to be stronger than the A'' fundamentals. If the plane of symmetry passed through a pair of carbon atoms, the B_{1u} and B_{2g} fundamentals have A' symmetry, while the B_{2u} fundamentals have A'' symmetry.

If this structure were correct, only one out of three possible A' fundamentals becomes active, but both A'' fundamentals. On the other hand, if the plane of symmetry passes through a pair of C=C bonds, the B_{2u} fundamentals have A' symmetry and the B_{1u} and B_{2g} fundamentals have A'' symmetry. Here, both A' fundamentals and one out of the three A'' fundamentals become active. This argument suggests to us that the halogen molecule interacts mainly with one of the C=C bonds, similarly to what was found for the ethylene chlorine complex [17]. The discussion of the combination bands given above is also consistent with the assumption that the A' vibrations are in general much stronger than the A'' vibrations. This assumption leads to the conclusion that the strong components of ν_{11} and ν_{19} both have A' symmetry. The combination bands of two

A' or of two A'' fundamentals have A' symmetry, while the combinations of A' and A'' have A'' symmetry. These considerations may explain why $\nu_{11}(A' + A'') + \nu_{19}(A' + A'')$ has two components, formed by the two strong and the two weak components of ν_{11} and ν_{19} , while $\nu_7(A'') + \nu_{19}(A' + A'')$ has only one. The $\nu_4(A') + \nu_{11}(A' + A'')$ combination involves the very strong ν_4 fundamental of benzene, which may explain why both components are active. There are a few other observations that may be made from table 3. First, the complex shifts are all rather small and, as expected, increase from chlorine to bromine to iodine chloride. The only benzene fundamentals which shift significantly are the CH out-of-plane bendings. The largest shift is observed for the E_{1g} fundamental (ν_{11}) where the A' component (accepting for the sake of argument the oblique structure with the halogen above a C=C bond) involves the motion of the four hydrogens closest to the plane of symmetry, while the two equivalent para hydrogens do not move. The A'' component, in contrast, involves mainly the motion of these two para hydrogens. For the E_{2u} fundamental the situation is reversed. The A' fundamental involves mainly the motion of the two equivalent para hydrogens, while in the A'' component, only the four hydrogens closest to the plane of symmetry are moving. It must be noted that both complex shifts and intensities are in accordance with what may be expected from these considerations, while for the other possible oblique structure one should expect similar shifts and intensities for both ν_{11} and ν_{19} .

5. CONCLUSIONS

The results of this investigation give very strong support for an oblique structure of the benzene chlorine, bromine and iodine chloride complexes. Considerations of intensities and complex shifts suggest that the halogen molecule interacts mainly with one of the C=C bonds of the benzene ring.

REFERENCES

- [1] MULLIKEN, R. S., 1950, *J. Am. chem. Soc.*, **73**, 600.
- [2] MULLIKEN, R. S., 1952, *J. Am. chem. Soc.*, **74**, 811.
- [3] COLLIN, J., and D'OR, L., 1955, *J. chem. Phys.*, **23**, 397.
- [4] D'OR, L., ALEWACTERS, R., and COLLIN, J., 1956, *Recl. Trav. chim. Pays-Bas Belg.*, **75**, 862.
- [5] MULLIKEN, R. S., 1955, *J. chem. Phys.*, **23**, 397.
- [6] FERGUSON, E. E., and MATSEN, F. A., 1958, *J. chem. Phys.*, **29**, 105.
- [7] FERGUSON, E. E., and MATSEN, F. A., 1960, *J. Am. chem. Soc.*, **82**, 3268.
- [8] FERGUSON, E. E., 1956, *J. chem. Phys.*, **25**, 577.
- [9] FERGUSON, E. E., 1957, *Spectrochim. Acta*, **10**, 123.
- [10] FERGUSON, E. E., 1957, *J. chem. Phys.*, **26**, 1357.
- [11] HASSEL, O., and STRØMME, K. O., 1958, *Acta chem. scand.*, **12**, 1146.
- [12] HASSEL, O., and STRØMME, K. O., 1959, *Acta chem. scand.*, **13**, 1781.
- [13] PERSON, W. B., COOK, C. F., and FRIEDRICH, H. B., 1967, *J. chem. Phys.*, **46**, 2521.
- [14] MULLIKEN, R. S., and PERSON, W. B., 1969, *Molecular Complexes* (Wiley-Interscience).
- [15] FREDIN, L., 1973, *Chem. Scripta*, **4**, 96.
- [16] FREDIN, L., and NELANDER, B., 1973, *J. molec. Struct.*, **16**, 205.
- [17] FREDIN, L., and NELANDER, B., 1973, *J. molec. Struct.*, **16**, 217.
- [17b] VOIGT, E. M., and MEYER, B., 1968, *J. chem. Phys.*, **49**, 852.
- [18] FREDIN, L., ROSENGREN, K. J., and SUNNER, S., 1973, *Chem. Scripta*, **4**, 93.

- [19] FREDIN, L., 1974, *Chem. Scripta* (in the press).
- [20] PLYLER, E. K., DANTI, A., BLAINE, L. R., and TIDWELL, E. D., 1960, *J. Res. natn. Bur. Stand.*, **64**, 29.
- [21] BRODERSEN, S., and LANGSETH, A., 1956, *Mat. Fys. Skr. Dan. Vid Selsk.*, **1**, No. 1.
- [22] HERZBERG, G., 1945, *Infrared and Raman Spectra* (Van Nostrand).
- [23] WILSON, E. B., 1934, *Phys. Rev.*, **45**, 706.
- [24] HOLLENBERG, J. L., and DOWS, D. A., 1962, *J. chem. Phys.*, **37**, 1300.
- [25] ZWERDLING, S., and HALFORD, R. S., 1955, *J. chem. Phys.*, **23**, 2221.
- [26] SWENSON, C. A., PERSON, W. B., DOWS, D. A., and HEXTER, R. M., 1959, *J. chem. Phys.*, **31**, 1324.
- [27] HERZBERG, G., 1950, *Spectra of Diatomic Molecules* (Van Nostrand).