

## Is the Benzene–Iodine Complex Really Axial?

L. Fredin and B. Nelander\*

*Contribution from the Thermochemistry Laboratory, Chemical Center, University of Lund, Lund, Sweden. Received October 13, 1973*

**Abstract:** Ir and uv spectra of nitrogen matrices containing benzene and iodine have been recorded. The results are compared with previous studies of benzene–halogen complexes. It is concluded that the benzene–iodine complex has an axial structure in contrast to other benzene–halogen complexes.

Ever since Mulliken published his first papers on donor–acceptor complexes,<sup>1,2</sup> many attempts have been made to find the structure of the benzene–halogen complexes.<sup>3–13</sup> As a result of the X-ray studies of Hassel and Strømme<sup>11,12</sup> and the ir spectroscopic investigations of Ferguson,<sup>8–10</sup> there now seems to be a general agreement that the free (1:1) benzene–halogen complexes have an axial structure.<sup>14,15</sup> The argument for the axial structure is based in part on the small changes in the ir spectrum of liquid benzene when halogens are added and in part on the structure of the crystalline complex. In both cases one is far from the isolated 1:1 complex for which theoretical predictions have been made. It would therefore be of interest to study benzene–halogen complexes in a situation where 1:1 complexes are known to be the dominating complex.

The matrix isolation technique in combination with ir spectral studies has been applied by many investigators to studies of hydrogen-bonded dimers<sup>16,17</sup> and complexes.<sup>18,19</sup> It appears to be a valuable tool also for studies of weak molecular complexes.<sup>20–22</sup> While one may argue about the influence of the matrix on the complex structure, it is at least possible to make sure that 1:1 complexes are studied. With these considerations in mind we recently studied the ir spectra of the chlorine, bromine, and iodine chloride complexes with benzene in a nitrogen matrix at 20°K.<sup>23</sup> The resulting

spectra suggest that all these complexes have an oblique structure<sup>5</sup> in solid nitrogen. The present paper extends this investigation to the benzene–iodine complex.

## Experimental Section

The cryostat used was described in ref 24. Pressures of benzene and iodine were measured in known volumes using a Rosemount capacitive pressure transducer (831A). They were mixed with nitrogen and the nitrogen pressure was measured with a bellows manometer (NAF 31880) calibrated against a mercury manometer. The gas mixture was deposited on a combined cesium iodide sapphire window, kept at  $20 \pm 0.1$ °K. In all experiments, except one (see Figure 1), ca. 45 mmol of gas mixture was deposited at a rate of  $1.5 \pm 0.005$  mmol/hr. The deposition rate was kept constant by two servo regulated metering valves.<sup>25</sup> Approximately 1 mmol of nitrogen was deposited before and after the deposition of the gas mixture. Ir spectra were recorded on a Perkin-Elmer 180 instrument, calibrated with standard gases.<sup>26</sup> Uv spectra were recorded on a Cary 15M. Nitrogen (L'Air Liquide A56 99.9996% 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 distilled on a vacuum line. Iodine (Merck p.a.) was sublimed under vacuum. (Note that the spectra of Figure 2 were reproduced directly from the recorded spectra and no wave number corrections were applied.)

## Results and Discussion

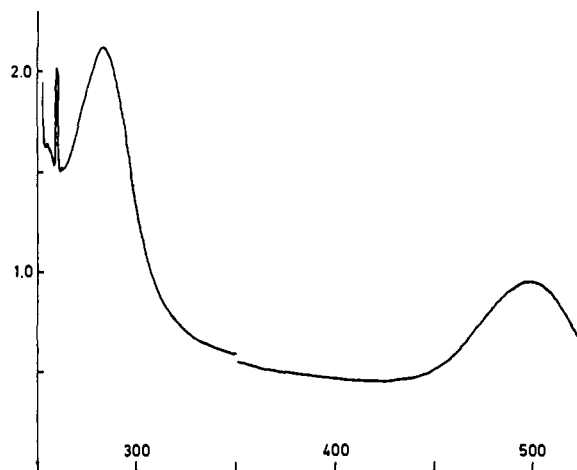
Figure 1 shows the uv spectrum of a nitrogen matrix containing both benzene and iodine. The charge-transfer absorption of the benzene–iodine complex is clearly seen, superimposed on the benzene and iodine spectra. Figure 2 gives a comparison between the ir spectra of matrices containing benzene, benzene and bromine, and benzene and iodine. Most forbidden benzene fundamentals become active for bromine-containing matrices, and their dependency on benzene and bromine concentration shows that they are caused by a 1:1 benzene–bromine complex. For the benzene–iodine complex only two forbidden benzene fundamentals become active,  $\nu_2(A_{1g})$  and  $\nu_{11}(E_{1g})$ .

(The fundamental frequencies of benzene were numbered as by Herzberg.<sup>27</sup>) In all other regions it only appears as if the broad and structureless absorption previously assigned<sup>23</sup> to benzene aggregates had been slightly enhanced.

It is interesting to compare the intensities of the  $A_{1g}$  and  $E_{1g}$  (the symmetry classification refers to free benzene) fundamentals of the bromine and iodine com-

- (1) R. S. Mulliken, *J. Amer. Chem. Soc.*, **72**, 600 (1950).
- (2) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).
- (3) J. Collin and L. D'Or, *J. Chem. Phys.*, **23**, 397 (1955).
- (4) L. D'Or, R. Alewacters, and J. Collin, *Recl. Trav. Chim. Pays-Bas*, **75**, 862 (1956).
- (5) R. S. Mulliken, *J. Chem. Phys.*, **23**, 397 (1955).
- (6) E. E. Ferguson and F. A. Matsen, *J. Chem. Phys.*, **29**, 105 (1958).
- (7) E. E. Ferguson and F. A. Matsen, *J. Amer. Chem. Soc.*, **82**, 3268 (1960).
- (8) E. E. Ferguson, *J. Chem. Phys.*, **25**, 577 (1956).
- (9) E. E. Ferguson, *Spectrochim. Acta*, **10**, 123 (1957).
- (10) E. E. Ferguson, *J. Chem. Phys.*, **26**, 1357 (1957).
- (11) O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, **12**, 1146 (1958).
- (12) O. Hassel and K. O. Strømme, *Acta Chem. Scand.*, **13**, 1781 (1959).
- (13) W. B. Person, C. F. Cook, and H. B. Friedrich, *J. Chem. Phys.*, **46**, 2521 (1967).
- (14) Cf. R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York, N. Y., 1969.
- (15) M. W. Hanna and J. L. Lippert, "Molecular Complexes," R. Foster, Ed., Elek Science, London, 1973.
- (16) M. Van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.*, **27**, 486 (1957).
- (17) A. J. Barnes and H. E. Hallam, *Quart. Rev., Chem. Soc.*, **23**, 392 (1969).
- (18) B. S. Ault and G. C. Pimentel, *J. Phys. Chem.*, **77**, 57 (1973).
- (19) B. S. Ault and G. C. Pimentel, *J. Phys. Chem.*, **77**, 1649 (1973).
- (20) L. Fredin, *Chemica Scripta*, **4**, 96 (1973).
- (21) L. Fredin and B. Nelander, *J. Mol. Struct.*, **16**, 205 (1973).
- (22) L. Fredin and B. Nelander, *J. Mol. Struct.*, **16**, 217 (1973).

- (23) L. Fredin and B. Nelander, *Mol. Phys.*, in press.
- (24) L. Fredin, Kj. Rosengren, and S. Sunner, *Chemica Scripta*, **4**, 93 (1973).
- (25) L. Fredin, *Chemica Scripta*, in press.
- (26) E. K. Plyler, A. Danti, L. R. Blaine, and E. D. Tidwell, *J. Res. Nat. Bur. Stand.*, **64**, 29 (1960).
- (27) G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, Princeton, N. J., 1945.



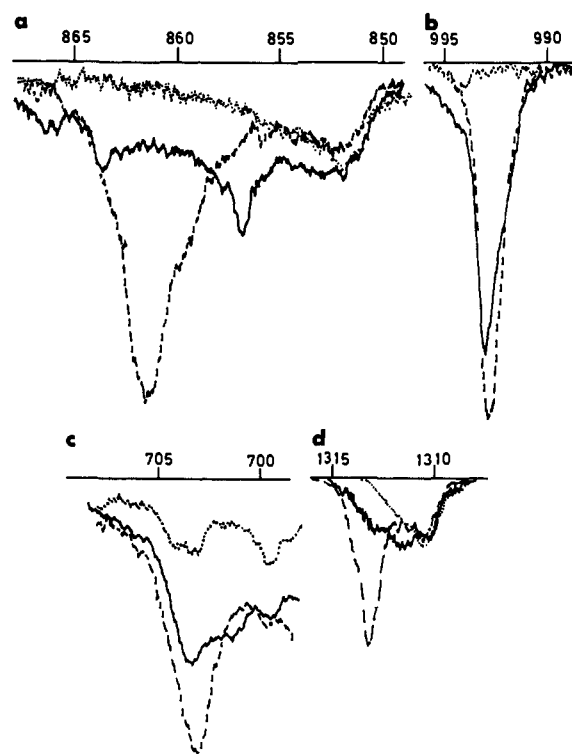
**Figure 1.** The uv-visible spectrum of a benzene- and iodine-containing nitrogen matrix ( $N_2:C_6H_6$  204,  $N_2:I_2$  588, millimoles deposited 22).

plexes, assuming that the complex concentrations are determined by the number of chance encounters between benzene and halogen molecules. While the  $A_{1g}$  absorptions are of comparable size, the  $E_{1g}$  absorption of the bromine complex is an order of magnitude larger.

The  $A_{1g}$  and  $E_{1g}$  fundamentals of benzene are the only ones that should become active if the iodine molecule is situated on the  $C_6$  axis of benzene. We therefore feel justified to interpret the results of this paper together with our previous results<sup>23</sup> as evidence for an axial complex geometry for the benzene-iodine complex. It may be noted that the low intensity of the  $E_{1g}$  fundamental of the benzene-iodine complex is understandable if the complex is axial. Then the transition dipole moment of this transition is parallel to the benzene plane, probably caused by the halogen-induced polarization of the benzene molecule as it deforms under an  $E_{1g}$  vibration. On the other hand, the transition dipole moment of the  $A_{1g}$  vibration is directed along the  $C_6$  axis, possibly being caused by the change in ionization potential of benzene as the ring size changes.<sup>6</sup>

For the benzene- $ICl$  complex<sup>23</sup> the  $ICl$  stretching region strongly suggested the existence of two different complexes with approximately equal concentrations. On the other hand, only one set of complex absorptions was found in the benzene part of the spectrum. This may now be understood, if we assume that one of the two isomeric benzene-iodine chloride complexes has chlorine closest to the benzene ring and an oblique structure (as the corresponding chlorine complex<sup>23</sup>), while the second isomer has an axial structure with iodine closest to the benzene plane. The first isomer should then be responsible for the appearance of most of the forbidden benzene fundamentals in the ir spectrum of the benzene and iodine chloride containing matrix. For the second isomer only the  $A_{1g}$  and  $E_{1g}$  fundamentals are allowed, the  $E_{1g}$  fundamental should be very weak, and the  $A_{1g}$  fundamental is probably too close to the  $A_{1g}$  fundamental of the first isomer to make it possible to resolve the difference (compare the positions of the  $A_{1g}$  fundamental for the iodine and iodine chloride complexes in Table I).

Our conclusions about complex geometries refer to complexes in a nitrogen matrix. It may therefore be



**Figure 2.** A comparison between the ir spectra of  $C_6H_6$ ,  $C_6H_6 \cdot Br_2$ , and  $C_6H_6 \cdot I_2$ : (—)  $N_2:C_6H_6$  91,  $N_2:I_2$  168, millimoles deposited 47; (---)  $N_2:C_6H_6$  93,  $N_2:Br_2$  158, millimoles deposited 42.5; (.....)  $N_2:C_6H_6$  93, millimoles deposited 48. (a) The  $\nu_{1g}(E_{1g})$  region of benzene. (b) The  $\nu_2(A_{1g})$  region of benzene. (c) The  $\nu_8(B_{2g})$  region of benzene. (d) The  $\nu_6(B_{2u})$  region of benzene.

**Table I.** A Comparison between the Ir Absorption Spectra of Some Benzene-Halogen Complexes

Assignment	$C_6H_6$	$C_6H_6 \cdot Cl_2$	$C_6H_6 \cdot Br_2$	$C_6H_6 \cdot ICl$	$C_6H_6 \cdot I_2$
2		991.5	990.8	988.7	990.9
4	678.6	688	687.7	693.1	690
8		703	702.4	701.3	
9		1311	1312.2	1314	
10			1151.0	1151	
11		858.0	860.5	866.6	855.6
		856.3 <sup>a</sup>	858.7 <sup>a</sup>	865.4 <sup>a</sup>	
13	1487.9	<i>b</i>	1482.1	1479.5	<i>b</i>
14	1039.8	1038	1036.9	1036.3	<i>b</i>
	1038.1			1034.8	
16	1607.4		1604.3	1604.7	
2 + 18	1589.1	1587.6	1585.8		
17	1180.0	1178	1178.5	1178.8	
18			606.7	606.1	
19		974	972.8	975.1	
			974 <sup>a</sup>	977 <sup>a</sup>	

<sup>a</sup> Shoulder. <sup>b</sup> Too strong overlap with the absorption of free benzene to allow observation of the complex absorption.

argued that the complex geometries we find are in part the result of matrix perturbations. However, in our opinion, such perturbations should lead to a distribution of complex geometries and consequently to broad ir absorption peaks. It must be remembered that the matrix is far from an ideal crystal, and the complexes are big compared to the nitrogen molecules, making it rather unlikely that the environment of all complexes of the same kind is identical. We therefore believe that our conclusions about benzene-halogen complex geometries are valid also outside a nitrogen matrix.