

Molecular Complexes of Benzene & Hexafluorobenzene with Carbon Dioxide & Carbon Disulphide: A Theoretical Study

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Received 19 September 1983; revised and accepted 24 February 1984

A CNDO/2 study has been carried out for the pairs of molecules given in the title and also for the individual molecules. The preferred configuration of each pair has been decided on the basis of energy calculations for various geometries. For the $C_6H_6 + CS_2$ pair the minimum energy corresponds to the configuration in which CS_2 molecule is along the six-fold C_6 -rotation axis of the benzene molecule. The minimum energy configuration for the $C_6H_6 + CO_2$ corresponds to the situation when the projection of the linear molecule is along the C_2 -axis passing through carbon atoms of the benzene molecule. The energy surface is found to be almost independent of the orientation of CS_2 above the C_6F_6 plane. For the $C_6F_6 + CO_2$ pair the minimum energy configuration corresponds to the geometry in which the CO_2 molecule is slipped over one of the -C-F bonds.

Unlike the solubility of carbon dioxide in alicyclic and aliphatic solvents, it is unusually large in aromatic liquids¹⁻⁷, due to specific interaction between CO_2 and aromatic molecules. The nature of this interaction is proposed to be of electron acceptor type by Hildebrand *et al.*⁸, whereas, Kohler⁹ suggests that it is due to quadrupole-quadrupole interaction. CNDO method has been applied to determine the nature of interaction and the geometry of the composite molecules¹⁰⁻¹⁶. Herein, we report the result of CNDO/2 calculations on 1:1 molecular complexes of benzene and hexafluorobenzene with carbon dioxide and carbon disulphide in order to elucidate their structures.

Method

The calculations were done using the CNINDO (QCPE No. 141) programme¹⁷ on a DEC 2050 machine. The spd basis set with Santry parameters¹⁸⁻²⁰ has been used for sulphur. The standard bond lengths and bond angles were used²¹.

Geometries

The following relative orientations of CO_2 or CS_2 with respect to hexafluorobenzene or benzene have been considered (see Fig. 1): (i) The C_∞ rotation axis of CO_2 or CS_2 lies parallel to the plane of benzene or hexafluorobenzene molecule in such a manner that C_6 -axis of benzene or hexafluorobenzene and C_2 -axis of CO_2 or CS_2 coincide. The projection of CO_2 or CS_2 makes an angle θ with the C_2 -axis of benzene or hexafluorobenzene passing through the carbon-carbon atoms. The angle θ is varied from 0 to 30° (due to symmetry all angular rotations are covered by this range).

(ii) The linear molecule CO_2 or CS_2 lies along the six-fold rotational axis of benzene or hexafluorobenzene.

(iii) The linear molecule CO_2 or CS_2 is perpendicular to the C_2 -axis of benzene or hexafluorobenzene passing through the carbon-carbon bond.

(iv) For the hexafluorobenzene and CO_2 pair we have also considered a geometry similar to (i) but the linear molecule is slipped over the C_2 -axis of C_6F_6 passing through carbon-carbon atoms.

Results and Discussion

The energy of stabilization, ΔE_{AB} defined by the equation $\Delta E_{AB} = E_{AB} - E_A - E_B$ was calculated in the CNDO framework for all the four pairs and for different configurations (i-iv) given in Fig. 1. The bond angles and bond lengths for the aromatic molecules have been kept intact. In all the adducts C-O and C-S

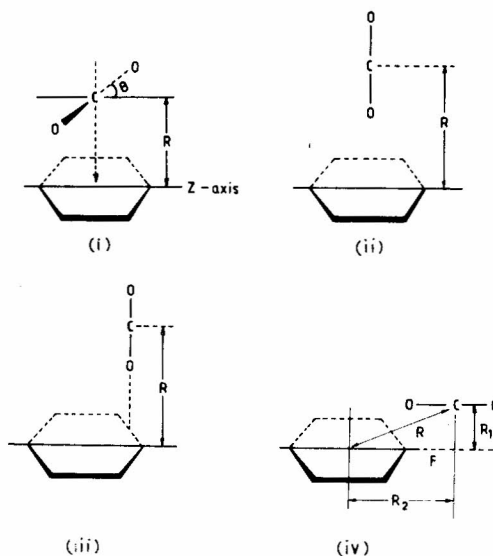


Fig. 1—Geometrical models for benzene + carbon dioxide/carbon disulphide and hexafluorobenzene + carbon dioxide/carbon disulphide pairs

bond lengths increase considerably from their corresponding values in the isolated molecules. The optimized geometries and charges on atom for isolated and composite molecules are given in Table 1.

Benzene + Carbon Dioxide

The most stable configuration is given by (i) in Fig. 1. Furthermore, the projection of CO₂ on benzene plane is aligned with the C₂-axis of benzene passing through the carbon-carbon atom (when θ is zero). $\Delta E_{(C_6H_6+CO_2)}$ is found to be minimum at intermolecular distance $R = 2.14\text{\AA}$ and when the C-O bond length is $1.24\text{\AA}$. The electron density values on individual atoms at the optimum internuclear separation indicate that there is very little charge transfer (0.025 electron) from benzene to carbon dioxide. In fact, there is only reorganisation of electronic charges on atoms in each molecule. This indicates that dipoles are induced by the field of quadrupole moment of the other molecules. The correlation of molecular orbitals of the composite molecule with the molecular orbitals of the individual molecules (benzene and carbon dioxide) shows that interaction of the HOMO play insignificant role in the stabilization.

Benzene + Carbon Disulphide

For this pair the most stable configuration is given by (ii) in Fig. 1, in agreement with an earlier work of similar nature²². It is interesting to mention here that this configuration is also favoured by the experimental study²³ of Rayleigh scattering of depolarised light from binary mixture in the liquid state. For this system

our calculations indicate charge transfer from benzene to carbon disulphide (0.103 electron). The transferred charge is delocalized over the entire carbon disulphide molecules.

Hexafluorobenzene + Carbon Dioxide

Unlike the benzene + carbon dioxide and benzene + carbon disulphide pairs the lowest energy configuration for hexafluorobenzene + carbon dioxide is less symmetrical. Although CO₂ is parallel to the plane of C₆F₆ it slips over one of the carbon-fluorine bonds as shown in Fig. 1(iv). This is possibly due to the strong polar character of C-F bond. Although the electronic charges on individual molecules are redistributed there is no intermolecular charge transfer. As in the case of benzene + carbon dioxide pair the interaction seems to be of electrostatic nature.

Hexafluorobenzene + Carbon Disulphide

For this pair the lowest energy configuration is the one in which CS₂ molecule is parallel to the plane of hexafluorobenzene molecule (Fig. 1(i)). The variation of $\Delta E_{(C_6F_6+CS_2)}$ is found to be almost independent of angle θ . In this case, charge is transferred (0.114 electron) from carbon atoms of hexafluorobenzene to carbon disulphide. This is due to the overlap of ²py and empty d-orbitals on CS₂ with the ²py orbitals in C₆F₆.

It is interesting to note that the experimental studies on the Rayleigh scattering of depolarized light for the mixture C₆H₆ + CS₂ and C₆F₆ + CS₂ suggest that in C₆H₆ + CS₂, CS₂ molecule is perpendicular to the

Table 1—Electron Density on Various Atoms in Isolated Molecules and Molecular Complexes for Optimised Geometry

Optimised geometry	Electron density on various atoms											
	Benzene + carbon dioxide											
(i) $R = 2.14\text{\AA}$ $\theta = 0^\circ$ $C-O = 1.24\text{\AA}$	3.967	4.011	4.011 (3.994)	3.967	4.011	4.011	0.999	1.001 (1.006)	1.001	0.999	1.002	1.002
	3.439 (3.463)	6.293 (6.268)	6.293 (6.268)									
Hexafluorobenzene + carbon disulphide												
(i) $R = 2.25\text{\AA}$ $C-S = 1.689\text{\AA}$	3.822	3.822	3.847 (3.842)	3.822	3.822	3.847	7.149	7.149 (7.158)	7.153	7.149	7.149	7.153
	3.912 (3.954)	6.101 (6.023)	6.101 (6.023)									
Hexafluorobenzene + carbon dioxide												
(iv) $R = 3.305\text{\AA}$ $R_1 = 2.20\text{\AA}$ $C-O = 1.24\text{\AA}$	3.812	3.851	3.832	3.850	3.832	3.851	7.167	7.163	7.160	7.160	7.160	7.163
	3.454	6.274	6.274									

Values within the parentheses indicate the electron densities in the isolated molecule

plane of benzene ring, whereas for the hexafluorobenzene + carbon disulphide pair, CS_2 is parallel to the hexafluorobenzene ring. Both these features are predicted by our theoretical calculations. Experimental results are not available for CO_2 + C_6H_6 and CO_2 + C_6F_6 mixtures to confirm the prediction.

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