

Structural Investigations of Liquid Binary Mixtures: Neutron Diffraction and Molecular Dynamics Studies of Benzene, Hexafluorobenzene, and 1,3,5-Trifluorobenzene

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The local structure in benzene-1,3,5-trifluorobenzene (BT), hexafluorobenzene-1,3,5-trifluorobenzene (HT), and benzene-hexafluorobenzene (BH) equimolar mixtures has been investigated by neutron diffraction experiment and molecular dynamics (MD) simulation. Experimentally it is found that the local order is very slightly affected in the temperature range investigated (298–346 K). The comparison between the present experimental data and those deduced from the assumption of ideality in using structure data on pure components revealed a variety of behaviors for the three mixtures investigated. When small differences are observed for the BT and FT mixtures, more significant deviations appear for the BH mixture. In this context, MD simulations indicate that in BT and FT mixtures each component tends to preserve its local structure (i.e., the one existing in the corresponding pure liquid), while between unlike molecules, C_6H_6 (or C_6F_6) and 1,3,5- $C_6H_3F_3$, the local structure appears as governed by the 1,3,5- $C_6H_3F_3$ molecules. In contrast, for the BH mixture a strong structural enhancement upon mixing occurs: well defined heterodimers, in a quasistacked configuration (intermolecular distance ~ 3.7 Å), are found. These heterodimers are also responsible of orientational correlations at larger distances (in the intermediate range, about 7–11 Å). Finally, the role of the competition between repulsive, dispersive, and electrostatic forces in the above mixtures is discussed in detail.

I. Introduction

After Patrick and Prosser¹ published evidence that near room temperature an equimolar mixture of benzene and hexafluorobenzene transforms into a solid compound whose melting point is 18 K higher than the melting points associated with the two pure components, a considerable effort was devoted to the investigation of fluorocarbon–hydrocarbon mixtures (for a review, see ref 2). Although it is now settled that the 1:1 C_6H_6 – C_6F_6 complex is at the origin of the columnar structure of the solid compound,³ it is more uncertain that this stacked configuration between unlike molecules subsists in the liquid phase. The existence of a 1:1 complex in the binary mixture is supported by the rather large deviations from ideality exhibited by thermodynamic properties,^{4–9} while various spectroscopic studies^{10–14} suggest that this complex, if present, is rather short lived. Furthermore, structural information coming from a neutron and X-ray diffraction study¹⁵ accredit the view of a preferential face to the face configuration between C_6H_6 and C_6F_6 molecules in the liquid mixture, a situation contrasting with that observed in the two pure liquids. Finally, and con-

trarily to what it was suggested in the early studies,¹ the cause of the charge transfer mechanism is not due to the origin of the specific fluorocarbon–hydrocarbon interaction but it is the quadrupolar contribution instead which provides the leading mechanism as indicated by further experimental^{8–16} and theoretical^{17–19} studies.

Recently we have investigated by neutron diffraction experiment and molecular dynamics simulation²⁰ the local structure in pure liquid benzene and its fluorinated derivatives, 1,3,5-trifluorobenzene and hexafluorobenzene. This study has shown that the short range order is very different in 1,3,5-trifluorobenzene as compared with the other two liquids and involves “dimers” in which the molecules are face to face with an intermolecular separation of the order of 4 Å.²¹ This situation is reminiscent of the benzene–hexafluorobenzene mixture discussed above. So to improve our understanding of the interactions between aromatic fluorocarbons and aromatic hydrocarbons we have investigated by neutron diffraction experiment and molecular dynamics simulation the following three binary mixtures: benzene–1,3,5-trifluorobenzene (BT), hexafluorobenzene 1,3,5-trifluorobenzene (HT), and benzene–hexafluorobenzene (BH), respectively. The main objective of this study is an attempt to rationalize the structural information

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obtained so far on the basis of a competition between repulsive, dispersive, and electrostatic interactions within the mixture. Thus, although the role of quadrupole–quadrupole forces is important to the understanding of the structure in these systems, the packing, the steric effects, and the dispersive forces are not negligible in this context. For instance, the existence of a stacked configuration between two nearest neighbors in 1,3,5-trifluorobenzene is the result of the cumulative effects of the packing, which is favored by the parallel configuration, of the dispersive effects, which are enhanced when the two molecules are face to face, and of the electrostatic forces at very short range which tend to stabilize the stacked configuration (for the peculiar charge distribution of the $C_6H_3F_3$ molecule, see Table 5 in ref 20). In fact we will show in the following that the investigation of the aforementioned binary mixtures can shed some light on the relation between liquid structure and intermolecular interactions in aromatic fluorocarbons and hydrocarbons mixtures.

II. Theoretical Background

The theory of a neutron diffraction experiment is well known and can be extended to a mixture of molecular liquids in using the formalism reported previously for neat molecular liquids.²⁰ Let us consider here a binary mixture of molecular liquids having a number density ρ and composed of two molecular species labeled 1 and 2, with a molar fraction x_1 and x_2 , respectively.

The corresponding total differential cross section per molecule $(d\sigma/d\Omega)_{\text{total}}$ is a sum of four contributions, namely,

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{total}} = \left(\frac{d\sigma}{d\Omega}\right)^{\text{incoh}} + \left(\frac{d\sigma}{d\Omega}\right)^{\text{self coh}} + \left(\frac{d\sigma}{d\Omega}\right)^{\text{dist}}_{\text{intra}} + \left(\frac{d\sigma}{d\Omega}\right)^{\text{dist}}_{\text{inter}} \quad (1)$$

The first two terms in expression 1 give rise to the so-called self-differential cross section

$$\left(\frac{d\sigma}{d\Omega}\right)^{\text{self}} = \sum_{i=1}^2 x_i \sum_{\alpha=1}^{N_i} [(b_{\alpha_i}^{\text{incoh}})^2 + b_{\alpha_i}^2] \quad (2)$$

where $b_{\alpha_i}^{\text{incoh}}$ and b_{α_i} are respectively the incoherent and the coherent scattering lengths of the nucleus α in the molecule i composed of N_i atoms. The last two terms in eq 1 are the distinct coherent cross section $(d\sigma/d\Omega)^{\text{dist coh}}$ where the relevant contribution at very large Q values comes almost exclusively from the intramolecular contribution.

The latter intramolecular contribution can be calculated as

$$\left(\frac{d\sigma}{d\Omega}\right)^{\text{dist}}_{\text{intra}} = \sum_{i=1}^2 x_i \sum_{\alpha \neq \beta_i}^{N_i} b_{\alpha_i} b_{\beta_i} j_0(Q r_{\alpha_i \beta_i}) \exp(-l_{\alpha_i \beta_i}^2 Q^2/2) \quad (3)$$

where $j_0(Q r_{\alpha_i \beta_i})$ is the spherical Bessel function of zero order, $r_{\alpha_i \beta_i}$ is the distance between the α and the β nuclei of the i molecule, $l_{\alpha_i \beta_i}$ is the corresponding root mean square fluctuation, and Q is the momentum transfer ($Q = 4\pi \sin \theta/\lambda$).

As for the last term in eq 1, it involves the coherent scattering due to the nuclei of the different molecules and gives, by Fourier transform, the intermolecular pair correlation function $g_{\text{inter}}(r)$

$$d_{\text{inter}}(r) = 4\pi\rho r [g_{\text{inter}} - 1] = \frac{1}{2\pi} \int \frac{Q}{\left(\sum_{i=1}^2 x_i \sum_{\alpha=1}^{N_i} b_{\alpha_i}\right)^2} \left(\frac{d\sigma}{d\Omega}\right)^{\text{dist}}_{\text{inter}} \sin Qr dQ \quad (4)$$

TABLE 1: Dependence upon the Temperature of the Density d of the Benzene–1,3,5-Trifluorobenzene, Benzene–Hexafluorobenzene, and Hexafluorobenzene–1,3,5-Trifluorobenzene Equimolar Mixtures ($d/\text{kg m}^{-3}$)

T/K	$C_6D_6-1,3,5-C_6D_3F_3$	$C_6D_6-C_6F_6$	$C_6F_6-1,3,5-C_6D_3F_3$
277	1162		
298	1131	1315	1459
346	1064	1223	1360

where $g_{\text{inter}}(r)$ is deduced from the partial pair correlation functions $g_{\alpha_i \beta_j}(r)$

$$g_{\text{inter}}(r) = \frac{\sum_{i,j=1}^2 x_i x_j \sum_{\alpha_i=1}^{N_i} \sum_{\beta_j=1}^{N_j} b_{\alpha_i} b_{\beta_j} g_{\alpha_i \beta_j}(r)}{\left(\sum_{i=1}^2 x_i \sum_{\alpha_i=1}^{N_i} b_{\alpha_i}\right)^2} \quad (5)$$

For the three equimolar mixtures investigated here, $g_{\text{inter}}(r)$ is a weighted sum of the partial correlation functions, namely,

$$g(r)_{C_6D_6-C_6D_3F_3} = 0.26 g_{CC} + 0.15 g_{DD} + 0.01 g_{FF} + 0.39 g_{CD} + 0.11 g_{CF} + 0.08 g_{FD} \quad (5a)$$

$$g(r)_{C_6D_6-C_6F_6} = 0.27 g_{CC} + 0.07 g_{DD} + 0.05 g_{FF} + 0.27 g_{CD} + 0.23 g_{CF} + 0.11 g_{FD} \quad (5b)$$

$$g(r)_{C_6F_6-C_6D_3F_3} = 0.28 g_{CC} + 0.02 g_{DD} + 0.11 g_{FF} + 0.14 g_{CD} + 0.36 g_{CF} + 0.09 g_{FD} \quad (5c)$$

III. Experimental and Data Reduction

1. Experimental Setup. The experiments were performed on the two-axial spectrometer 7C2,²² situated on the hot source of the Orphée reactor at the Laboratoire Léon Brillouin (Laboratoire Commun CEA-CNRS, Saclay, France). The use of an incident neutron wavelength $\lambda = 0.7 \text{ \AA}$ combined with the multidetector allowed us to perform measurements in the Q range $0.4\text{--}16 \text{ \AA}^{-1}$.

Equimolar mixtures have been prepared using deuterated benzene (>99.95% in deuterium) and hexafluorobenzene, both originating from Aldrich. The 1,3,5-trifluorobenzene was synthesised and the isotopic purity (97.8%) was checked using NMR spectrometry.

The density of the mixtures has been estimated under the assumption of the additivity of the molar volumes of the neat liquids²⁰ (see Table 1). Furthermore, we assumed that the molar volumes of the hydrogenated and deuterated compounds were the same.

The sample was held in a vanadium cylindrical container (0.1 mm thick) with an inner diameter of 6 mm and was placed in the 45 mm high neutron beam. The cell was mounted in a thermostat and heated from a temperature close to the melting point of the mixture up to a temperature just below its boiling point (see Table 1). The temperature of the sample was kept constant, within $\Delta T = 0.2 \text{ K}$, during the runs.

Independent measurements of the empty cell, of the background and of a vanadium rod were performed. Several runs were accumulated (typically 10 for the sample and the container, 6 for the vanadium rod and for the background) of 10^6 monitor counts.

A typical diffraction pattern obtained for the mixture benzene–1,3,5-trifluorobenzene and for the empty cell is reported in

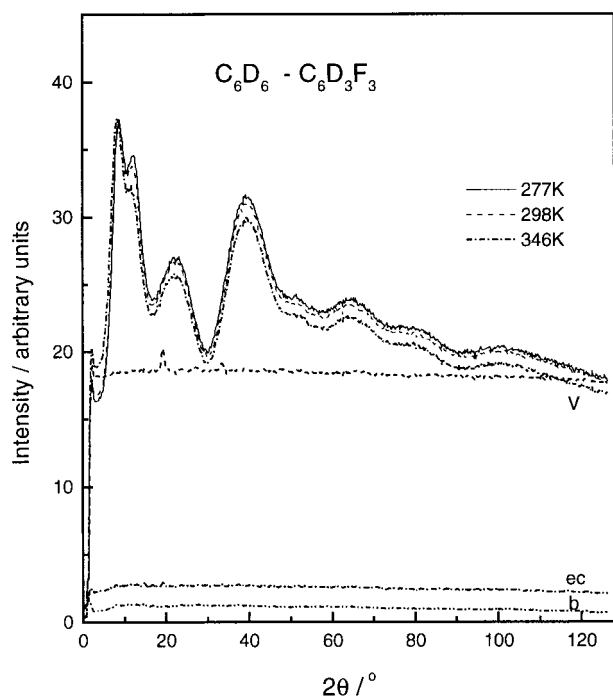


Figure 1. Experimental scattered intensities of the liquid mixture C_6D_6 -1,3,5- $C_6D_3F_3$ at the three investigated temperatures. The background (b), the vanadium (V), and the empty cell (ec) runs are reported.

Figure 1. The background and the vanadium runs are also displayed for comparison.

2. Data Reduction. Corrections for background, container scattering, and self-absorption were carried out using conventional methods²³ based upon Paalman and Pings' formalism²⁴ and for multiple scattering using the isotropic approximation of Blech and Averbach.²⁵ The corrected data have been scaled to absolute units using the vanadium intensities as a standard. The corrected differential cross section of the three binary mixtures at room temperature are displayed in Figure 2, showing that inelasticity effects are present for all the mixtures. The inelasticity corrections have been performed using the method previously described²⁰ for the neat liquids. Let us remind that the total differential cross section may be written as

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{total}}^{\text{exp}} = \left(\frac{d\sigma}{d\Omega}\right)_{\text{intra}}^{\text{dist}} + \left(\frac{d\sigma}{d\Omega}\right)_{\text{inter}} + \left(\frac{d\sigma}{d\Omega}\right)^{\text{self}} [1 + P(Q)] \quad (6)$$

where inelasticity contributions to the distinct terms have been neglected. In this equation the intermolecular contribution $(d\sigma/d\Omega)_{\text{inter}}$ becomes negligible for Q values greater than about 5 \AA^{-1} . The intramolecular contribution $(d\sigma/d\Omega)_{\text{intra}}^{\text{dist}}$ was calculated from the expression 3 using the parameters associated with the pure components involved in the mixtures (see Table 2 in ref 20). Finally, $P(Q)$ in eq 6 was taken as $P(Q) = A + BQ^2 + CQ^4$.²⁰

IV. Main Observations

The distinct coherent cross section obtained from the three mixtures at the two extremes of the temperature range are reported in Figure 3, as well as the calculated intramolecular contribution (eq 3). It appears that, for Q greater than 6 \AA^{-1} , the scattering is mainly due to the intramolecular contribution. Furthermore, this contribution is found to be practically temperature independent. We have to point out that these two findings were also observed with the neat liquids which compose the mixtures.²⁰

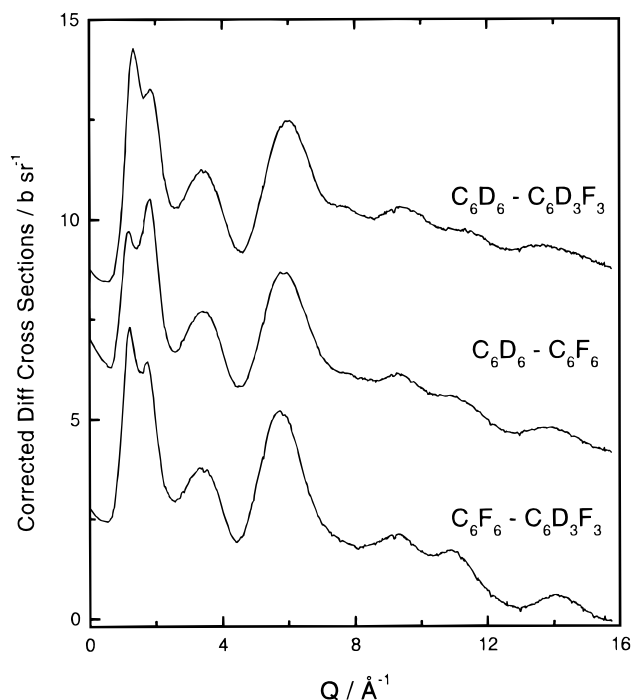


Figure 2. Corrected differential cross sections of the three liquid mixtures at room temperature. For clarity, the curves are shifted: +5 for the C_6D_6 -1,3,5- $C_6D_3F_3$ mixture, -5 for the C_6F_6 -1,3,5- $C_6D_3F_3$ mixture.

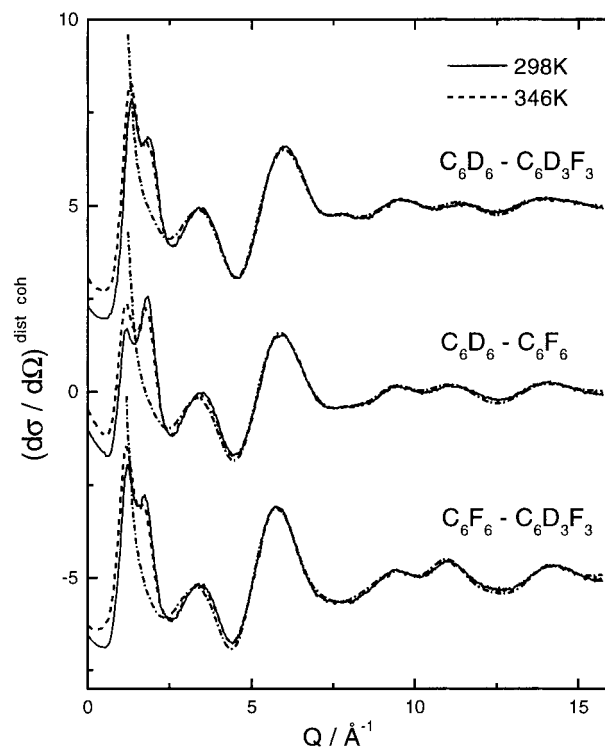


Figure 3. Coherent (distinct) cross section of the three liquid mixtures at 298 and 346 K. The contribution of the calculated (---) distinct intramolecular cross section (temperature independent, see text) is also reported. For clarity, the curves are shifted: +5 for the C_6D_6 -1,3,5- $C_6D_3F_3$ mixture, -5 for the C_6F_6 -1,3,5- $C_6D_3F_3$ mixture.

Notice that the intramolecular cross section for the pure components has been estimated by fitting the Q -weighted distinct cross section in the range 4 – 15.8 \AA^{-1} in adjusting the atomic parameters figuring in eq 3. The fit was obtained by minimising an agreement factor R , as previously described (see expression 15 in ref 20). For the mixtures, the number of

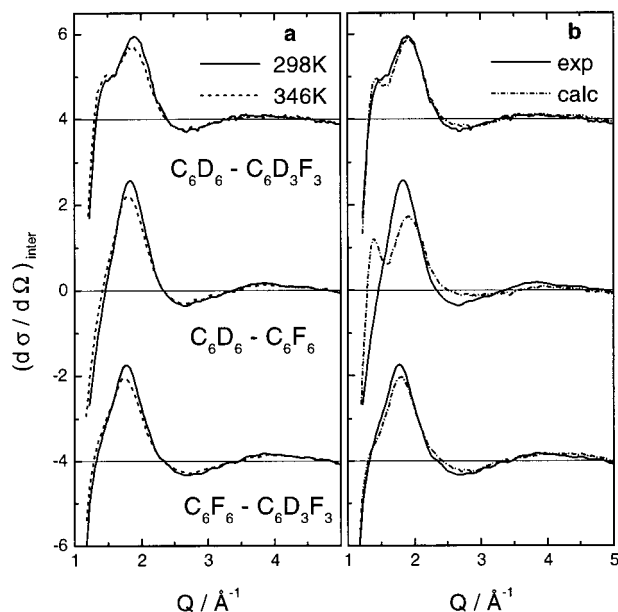


Figure 4. Intermolecular cross section of the three liquid mixtures: (a) experimental $(d\sigma/d\Omega)_{\text{inter}}$ at 298 and at 346 K; (b) experimental and calculated functions (assuming ideality, see text) at 298 K. For clarity, the curves are shifted: +4 for the C_6D_6 -1,3,5- $\text{C}_6\text{D}_3\text{F}_3$ mixture, -4 for the C_6F_6 -1,3,5- $\text{C}_6\text{D}_3\text{F}_3$ mixture.

parameters is too large to allow us an adjustment as accurate as the one obtained in the case of the pure components. Hence we have preferred to use the linear combination of the intramolecular cross sections deduced from the study of the pure components. In practice the R -factor associated with the mixture has values (0.11–0.12) of the same magnitude than those obtained for the pure components (see Table 2 in ref 20). Moreover these values do not significantly change with temperature in the range investigated.

After removal of the above intramolecular contribution, the intermolecular cross sections can be obtained: they are reported for the three mixtures in Figure 4a. First of all it appears that the structure is only slightly affected in the temperature range. Moreover, these modifications are observed in a very limited Q range centred around the main peak at about 2 \AA^{-1} . Similar findings were reported also for the neat liquids.²⁰

In a first approach we have calculated, for all the mixtures, the intermolecular cross sections supposing the additivity (i.e., ideality) of the intermolecular cross sections of the components in the mixture, namely,

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{inter}}^{\text{calc}} = \sum_{i=1}^2 x_i \left(\frac{d\sigma}{d\Omega}\right)_{\text{inter}_i} \quad (7)$$

The comparison between the calculated and the experimental intermolecular cross section, at room temperature, is presented in Figure 4b. In spite of small discrepancies, a good agreement is observed between the two cross sections for the BT and HT mixtures.

In marked contrast, the BH mixture exhibits a very different behaviour from the two others. Clearly, the doublet structure observed in the calculated intermolecular cross section at about 1.5 – 2 \AA^{-1} , which is reminiscent of the doublet structure existing in the two neat liquids,²⁰ is not observed in the experimental intermolecular cross section for this mixture. From this simple finding, we can conclude that the structure in the BH mixture is very different from the one which exists in the corresponding neat liquids.

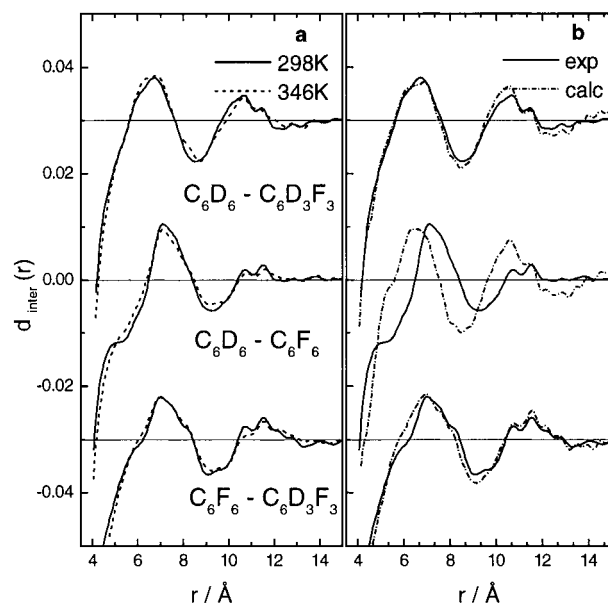


Figure 5. Intermolecular pair correlation function $d_{\text{inter}}(r)$ of the three liquid mixtures: (a) experimental function at 298 and 346 K; (b) experimental and calculated (assuming ideality, see text) functions at room temperature. For clarity, the curves are shifted: +0.03 for the C_6D_6 -1,3,5- $\text{C}_6\text{D}_3\text{F}_3$ mixture, -0.03 for the C_6F_6 -1,3,5- $\text{C}_6\text{D}_3\text{F}_3$ mixture.

The question of the local ordering in the mixtures is better appreciated using a r -space representation, namely the pair correlation function $d_{\text{inter}}(r)$. This function, obtained after Fourier transform of the intermolecular differential cross section $(d\sigma/d\Omega)_{\text{inter}}$ (see eq 4) is presented for the three mixtures at two temperatures (Figure 5a). Here again the temperature dependence is weak. The mixtures display two shells of neighboring molecules but it is for the BT mixture that the second shell is the most pronounced (Figure 5a). The most remarkable features are observed for the BH mixture, which presents a first shell composed of a pronounced shoulder at about 5 \AA and a peak centered around 7 \AA while the second shell of neighbors is barely visible. It comes out from these simple observations that in the BH mixture a more packed structure is detected at short distances, whereas the translational order seems less spatially extended.

The Fourier transforms of the calculated intermolecular cross sections have been performed for the mixtures at room temperature and are displayed in Figure 5b together with the experimental ones. The same overall good agreement between calculated and experimental $d_{\text{inter}}(r)$ function for the BT and HT mixtures is observed, while in contrast, the calculated pair correlation function is markedly different from the experimental one for the BH mixture. These observations complement those reported just above on the comparison using the Q -space representation.

The differences between these mixtures can be better emphasised in using the “excess function” $h_{\text{exc}}(r)$ which is the Fourier transform of the excess intermolecular cross section defined as

$$h_{\text{exc}}(r) = \frac{1}{2\pi^2 \rho r} \int \frac{Q}{\left(\sum_{i=1}^2 x_i \sum_{\alpha_i=1}^{N_i} b_{\alpha_i}\right)^2} \times \left[\left(\frac{d\sigma}{d\Omega}\right)_{\text{inter}} - \left(\frac{d\sigma}{d\Omega}\right)_{\text{inter}}^{\text{ideal}} \right] \sin Qr dQ \quad (8)$$

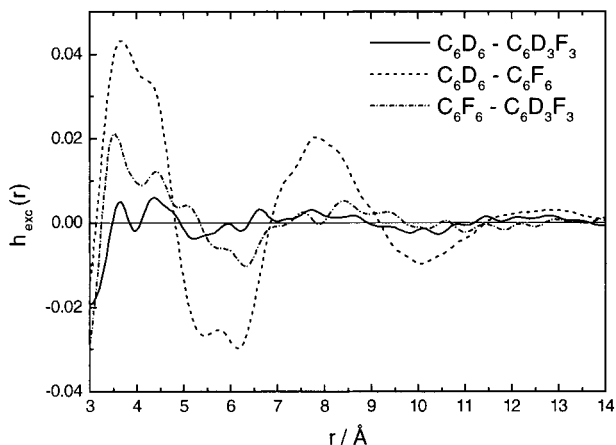


Figure 6. Inter-molecular pair correlation “excess” function $h_{\text{exc}}(r)$ of the three liquid mixtures at room temperature (see text).

and which is reported for the three mixtures in Figure 6. In this representation the deviations from zero appear rather small for the HT mixture and immaterial for the BT mixture, whereas for the BH mixture marked deviations are observed in all the r -domain investigated. In particular, the latter features suggest that a structural enhancement takes place in the two first shells of neighbors within the BH mixture.

V. Molecular Dynamics Simulation

1. Computational Details. In the present study, the structural properties of the aforementioned binary mixtures have been calculated, at room temperature, by molecular dynamics (MD) simulation in the microcanonical ensemble. The MD runs have been performed in the following conditions. Each simulated system was composed of $N = 256$ molecules in a cell of volume equal to $L^3 = V_{\text{molar}} N/N_A$. Using periodic boundary conditions, the molecular trajectories were solved by a “leap-frog” algorithm with a time step of 10^{-2} ps, the rotational motions of the molecules being treated in the framework of the quaternions formalism. The cut-off radius of the intermolecular forces was equal to half of the box edge, whereas the long range corrections for the repulsive and dispersive contributions were added to the pressure and the internal energy. For each mixture, the physical properties calculated in our simulations have been averaged over a MD run of 600 ps long, after an equilibration time of about 75 ps.

The intermolecular potential energy is given by a sum of atom–atom contributions:

$$U_{\alpha\beta}(r) = B_{\alpha\beta} \exp(-C_{\alpha\beta} r_{\alpha\beta}) - A_{\alpha\beta} r_{\alpha\beta}^{-6} + q_{\alpha} q_{\beta} r_{\alpha\beta}^{-1} \quad (9)$$

where α and β label the C, H, and F atoms, respectively, and $r_{\alpha\beta}$ is the distance between the atoms α and β belonging to two different molecules of the fluid. Values of the partial charges q_{α} are closer to reproduce the experimental quadrupole moment of the molecule or are deduced from ab initio calculations while the cross potential parameters are calculated from the usual combination rules $B_{\alpha\beta} = (B_{\alpha\alpha} B_{\beta\beta})^{1/2}$, $C_{\alpha\beta} = 1/2 (C_{\alpha\alpha} + C_{\beta\beta})$, and $A_{\alpha\beta} = (A_{\alpha\alpha} A_{\beta\beta})^{1/2}$ and the values assigned to the A, B, and C parameters are in general determined from an energy minimisation of the crystal structure.

The potential parameters and the molecular charge distributions used in the present simulations of binary mixtures are those discussed in our previous paper devoted to the structural properties of the neat liquids (see Tables 4 and 5 in ref 20). Let us emphasize that for the mixtures involving the 1,3,5-trifluoro-

TABLE 2: Simulated Thermodynamics Properties at Room Temperature^a

mixture	x_{Bz}/mf	$U/\text{kJ mol}^{-1}$	$U^E/\text{kJ mol}^{-1}$	$\Delta P/\text{MPa}$
BT	0.5	−30.8	+0.9 (+0.496)	+30
HT	0.5	−30.8	+0.4 (−0.043)	+6
BH	0.25	−35.6	−2.7 (−0.456)	+6
	0.50	−37.0	−3.8 (−0.496)	+13
	0.75	−35.9	−2.5 (−0.178)	+16

^a U the internal energy of the mixture and U^E the excess energy of mixing which express the deviation from U of the ideal mixture; ΔP the pressure difference between the pressure of the simulated mixture and that of the ideal mixture. Both systems having the same numerical density (that of the ideal mixture). (The experimental excess enthalpy measured by Fenby and Scott⁶ are presented, for comparison, in parentheses.)

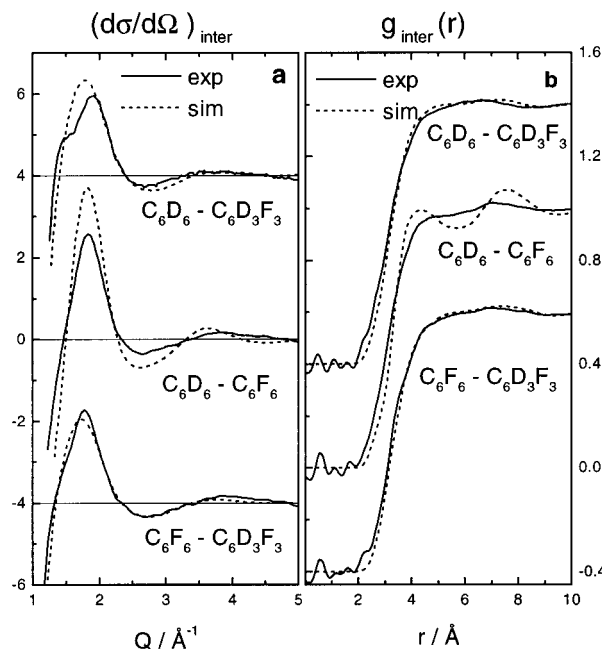


Figure 7. Comparison between (—) experimental and (---) simulated intermolecular functions at room temperature for the three liquid mixtures: (a) differential cross section $(d\sigma/d\Omega)_{\text{inter}}$; (b) pair correlation function $g_{\text{inter}}(r)$. For clarity the curves are shifted ± 4 in (a) and ± 0.4 in (b), “+” for the C_6D_6 –1,3,5- $\text{C}_6\text{D}_3\text{F}_3$ mixture, and “−” for the C_6F_6 –1,3,5- $\text{C}_6\text{D}_3\text{F}_3$ mixture.

benzene the models 1 and 2 (described in details in ref 20) have been checked in this study. However, the differences in structure generated by the two models are negligible and only the MD results using the model 1 will be presented and discussed here. The thermodynamics properties calculated for the three mixtures near room temperature are listed in Table 2. The excess internal energy U^E and the excess pressure ΔP which characterize the departure of these quantities from the corresponding values evaluated for an ideal mixture are presented more precisely. For equimolar mixtures, the experimental trends as deduced from the excess enthalpy data of Fenby and Scott (ref 6) are well reproduced by the simulations, namely, U^E decreases from a positive value to a negative value in going from the BT mixture to the BH mixture, in passing by the intermediate situation of the HT mixture. Moreover, for the BH mixture a minimum of U^E is found near $x_{\text{Bz}} = 0.5$ (mole fraction (mf) of benzene) instead of ~ 0.4 as observed experimentally.⁶ However, the order of magnitude of the departure from ideality is generally too strong and particularly for the BH mixture, a result which is not unexpected considering first that no effort has been devoted to reparametrize the potential parameters for

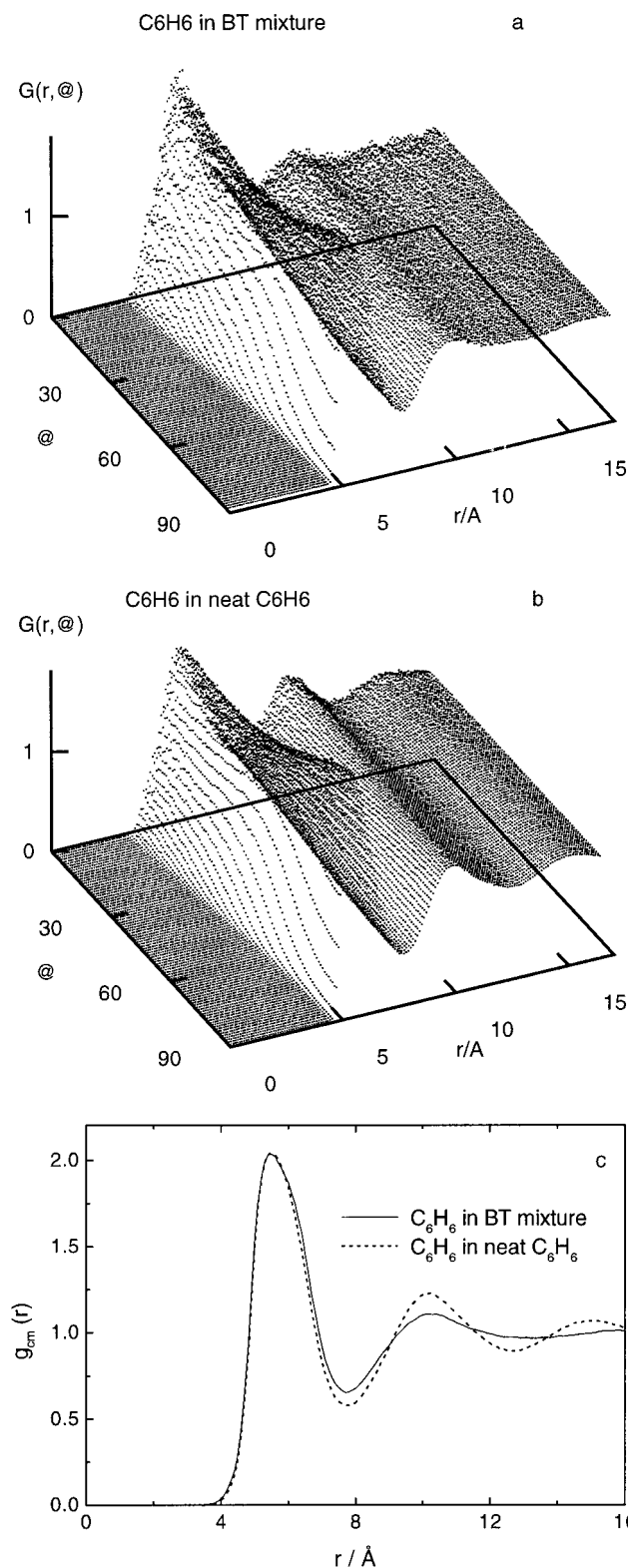


Figure 8. Pair correlation function of a pair of benzene molecules at room temperature: (a) $G(r, \theta)$ function in the equimolar benzene-1,3,5-trifluorobenzene (BT) mixture; (b) $G(r, \theta)$ function in the neat liquid benzene; (c) $g_{cm}(r)$ function of the center of mass. (—) in the BT mixture and (---) in the neat liquid benzene.

the mixtures and next that the density of the simulated mixtures was identified to that of the ideal mixture. Hence, with respect to the latter point, the reported excess pressure ΔP is an indirect measure of the excess molar volume of mixing (a positive excess pressure corresponds to a positive excess molar volume as it is observed experimentally with the BH mixture²). So some care

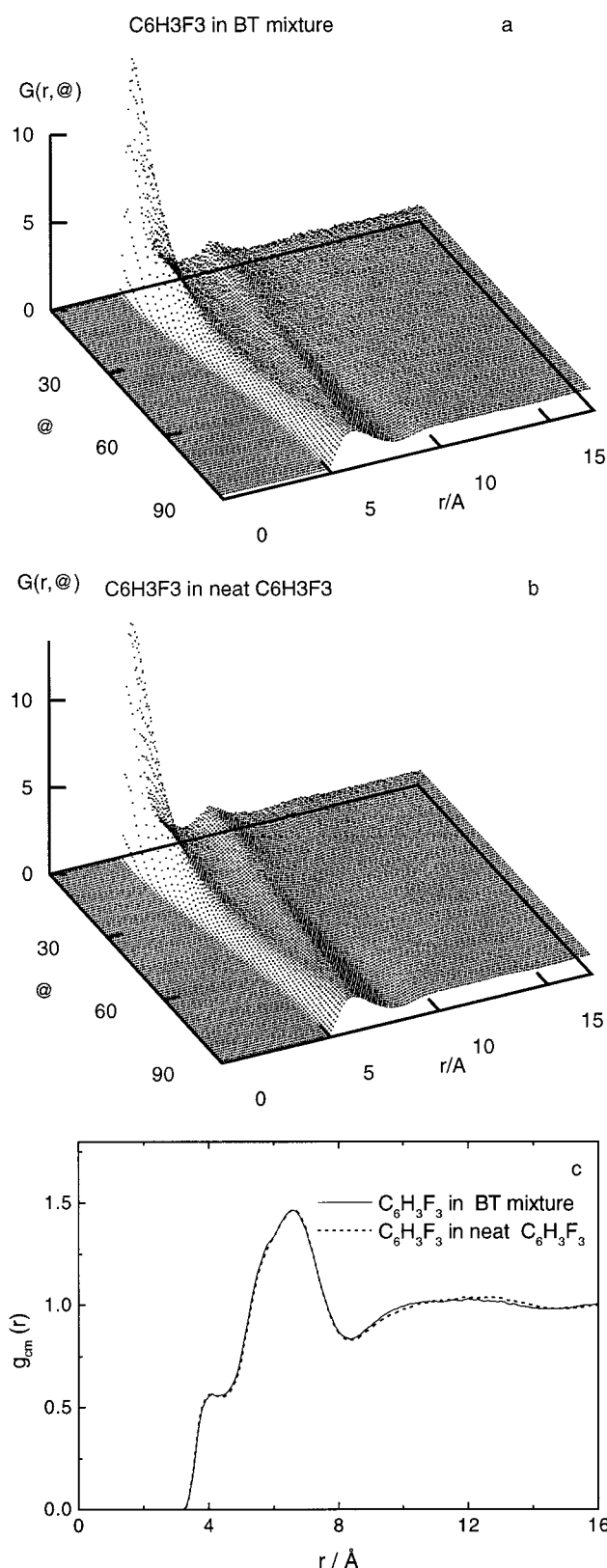


Figure 9. Pair correlation function of a pair of 1,3,5-trifluorobenzene molecules at room temperature: (a) $G(r, \theta)$ function in the equimolar benzene-1,3,5-trifluorobenzene (BT) mixture; (b) $G(r, \theta)$ function in the neat liquid 1,3,5-trifluorobenzene; (c) $g_{cm}(r)$ function of the center of mass. (—) in the BT mixture and (---) in the neat liquid 1,3,5-trifluorobenzene.

must be taken in comparing experimental data and simulation results as it stands. Whatsoever it may be, in the case of the BH mixture we do feel that the internal energy of mixing is

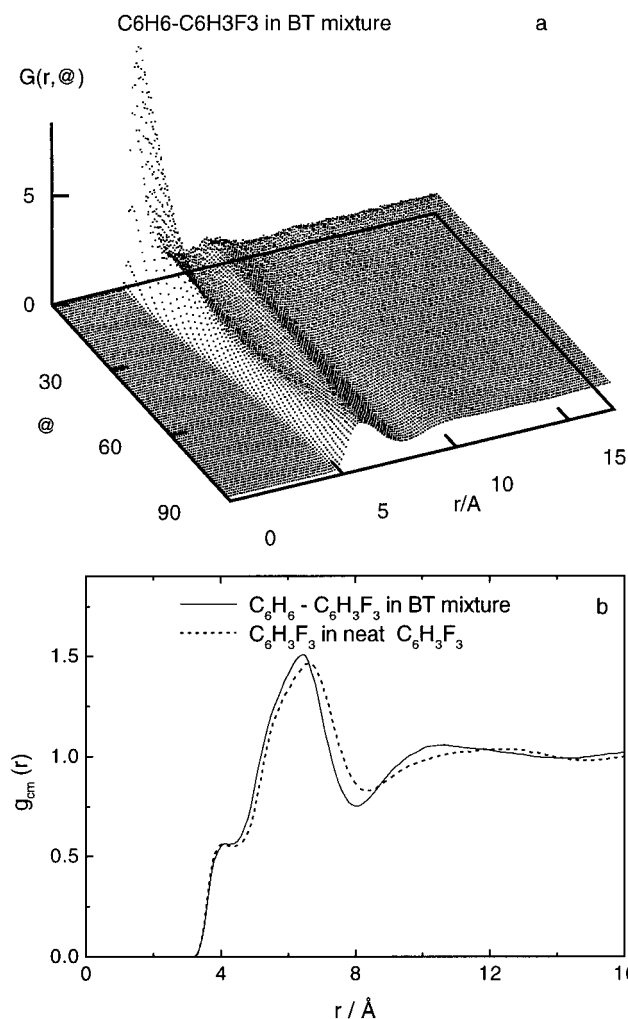


Figure 10. Pair correlation function of a pair of benzene-1,3,5-trifluorobenzene molecules at room temperature: (a) $G(r, \theta)$ function in the equimolar benzene-1,3,5-trifluorobenzene (BT) mixture; (b) $g_{cm}(r)$ function of the center of mass, (—) in the BT mixture and (---) in the neat liquid 1,3,5-trifluorobenzene.

too negative with the above potential parameters and some improvement could be reached in that direction.

2. Comparison between Neutron Diffraction and Molecular Dynamics Results. The comparison between neutron diffraction and molecular dynamics simulations for the intermolecular scattering cross sections is presented at room temperature in Figure 7a. One notices that although an overall agreement between the experimental and the simulation results is observed for the three mixtures, some discrepancies show up. For the BT mixture, the shoulder existing at about 1.5 \AA^{-1} is not resolved in the simulation and for the BH mixture the magnitude of the main peak is more intense in the simulation than in the experiment. On the other hand a very good agreement is obtained for the HT mixture.

If we consider now the intermolecular pair correlation function $g_{inter}(r)$ at room temperature, a better agreement is obtained (Figure 7b). For the BT and the FT mixtures the main features observed in the experimental functions $g_{inter}(r)$ are well reproduced. For the BH mixture there exist marked oscillations in the simulated function which appear more damped in the experimental data. This overstructuration is generated by the intermolecular potential model used to describe the BH mixture (see the previous discussion on the internal energy of mixing). In particular the dispersion contribution in our model of potential energy which was deduced from the investigation of the pure

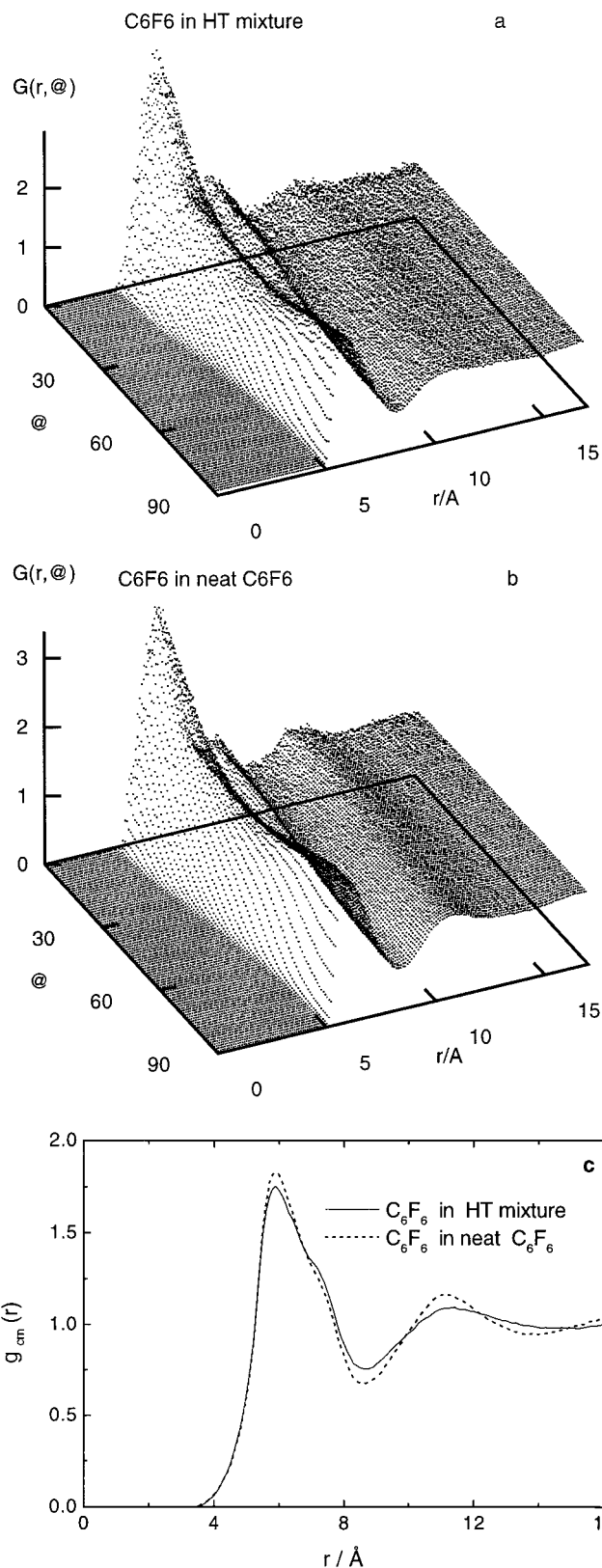


Figure 11. Pair correlation function of a pair of hexafluorobenzene molecules at room temperature: (a) $G(r, \theta)$ function in the equimolar hexafluorobenzene-1,3,5-trifluorobenzene (HT) mixture; (b) $G(r, \theta)$ function in the neat liquid hexafluorobenzene; (c) $g_{cm}(r)$ function of the center of mass, (—) in the HT mixture and (---) in the neat liquid hexafluorobenzene.

liquids cannot take properly into account the contributions coming from electronic correlation effects between unlike species. Indeed it is well known from ab initio studies¹⁹ that

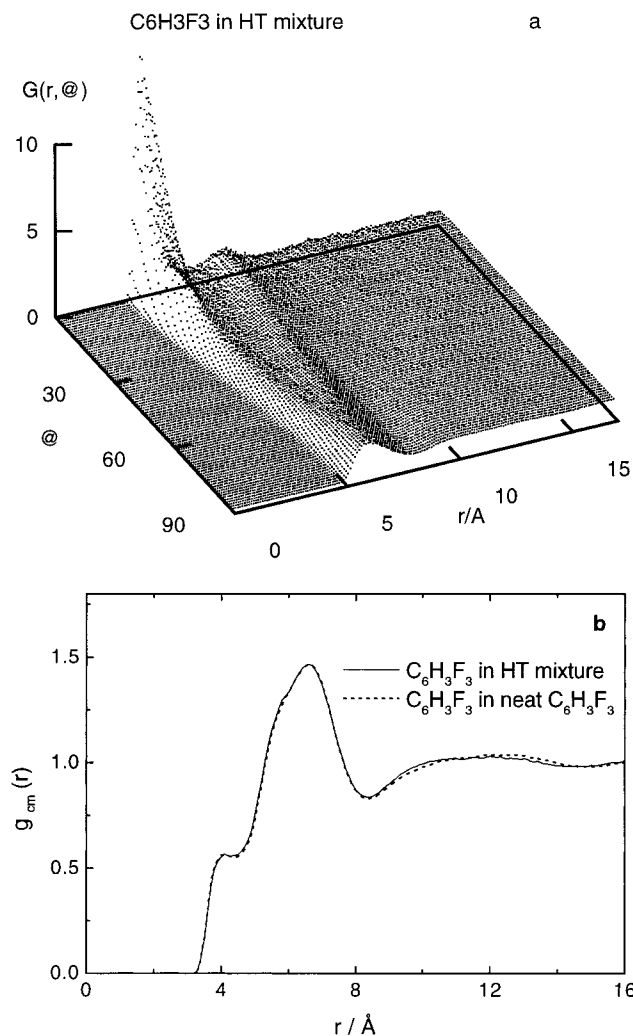


Figure 12. Pair correlation function of a pair of 1,3,5-trifluorobenzene molecules at room temperature: (a) $G(r, \theta)$ function in the equimolar hexafluorobenzene–1,3,5-trifluorobenzene (HT) mixture; (b) $g_{cm}(r)$ function of the center of mass, (—) in the HT mixture and (---) in the neat liquid 1,3,5-trifluorobenzene.

these effects contribute significantly to the energy of stabilization of van der Waals complexes and especially for the BH complex in a stacked configuration. Therefore, in the absence of a damping of the dispersion contributions at the short distances involved by the complex formation an overestimation of the structural enhancement of the corresponding liquid mixture is expected. Although it is possible to introduce in an ad hoc way such a damping in our model potential for C_6H_6 – C_6F_6 interactions, we have not pursued along this line. Instead and keeping in mind the above limitation we have preferred to continue to analyse our neutron data at the light of the present MD simulations.

VI. Discussion

Information on the local order existing in the investigated mixtures can be obtained from the MD simulations in using the partial pair correlation functions (pcf) $g_{ij}(r)$ calculated for each system and with the help of the angular pcf $G(r, \theta)$ defined as

$$\rho G(r, \theta) = \frac{1}{N} \left\langle \sum_{i \neq j}^N \delta(r - r_{ij}) \delta(\theta - \theta_{ij}) \right\rangle \quad (10)$$

This function allows us to quantify the orientational correlation of a pair of molecules i and j having their center of mass

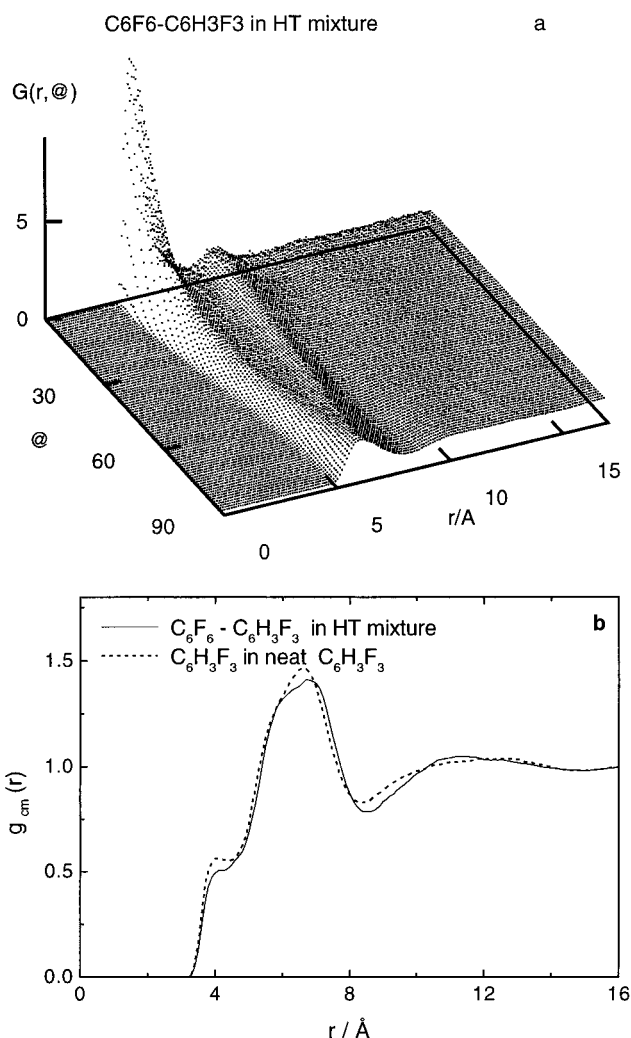


Figure 13. Pair correlation function of a pair of hexafluorobenzene–1,3,5-trifluorobenzene molecules at room temperature: (a) $G(r, \theta)$ function in the equimolar hexafluorobenzene–1,3,5-trifluorobenzene (HT) mixture; (b) $g_{cm}(r)$ function of the center of mass, (—) in the HT mixture and (---) in the neat liquid 1,3,5-trifluorobenzene.

separated by a distance r_{ij} and where the angle between their symmetry axes of highest order is θ_{ij} .

First we will discuss the case of the mixtures which do not exhibit a structural enhancement upon mixing, namely, the BT and the HT mixtures. Moreover, since with the BT and HT mixtures, the simulated functions $G(r, \theta)$ and $g_{ij}(r)$ do not reveal any significant concentration dependence, only the results obtained with the equimolar mixtures are discussed hereafter.

1. Benzene–1,3,5-Trifluorobenzene Mixture. The angular pair correlation function $G(r, \theta)$ between benzene molecules in the BT mixture (Figure 8a) appears fairly similar to the one that we have reported²⁰ in neat liquid benzene (Figure 8b). An almost isotropic order is reached at distances greater than 5 \AA . On the basis of our previous analysis, we come to the conclusion that parallel configurations of the molecules are again favored at very short distances in the mixture. In contrast, the second shell of neighboring benzene molecules is now more strongly damped. This observation is well illustrated in comparing the center of mass–center of mass distribution function $g_{cm}(r)$ of the benzene molecules in the neat liquid and in the mixture (Figure 8c), respectively.

If we consider now the simulated functions $G(r, \theta)$ and $g_{cm}(r)$ associated with the 1,3,5-trifluorobenzene molecules in the BT mixture, we see in Figure 9 that they exhibit practically no

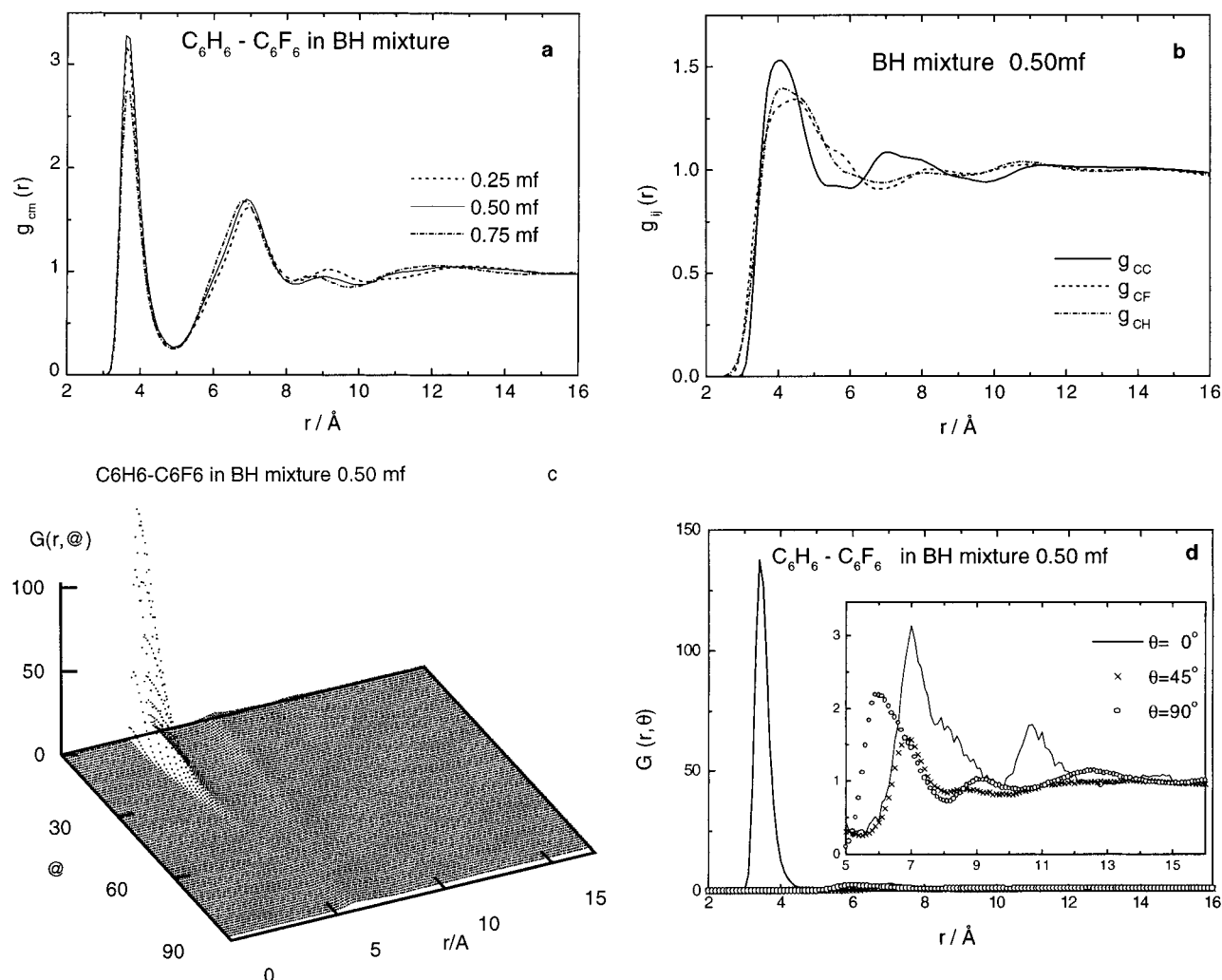


Figure 14. Pair correlation function of a pair of benzene-hexafluorobenzene molecules at room temperature: (a) dependence upon the concentration of the $g_{cm}(r)$ function of the center of mass in the benzene-hexafluorobenzene (BH) mixtures: (---) 0.25 mf, (—) 0.50 mf, and (-·-) 0.75 mf in benzene; (b) atom-atom correlation functions $g_{CC}(r)$, $g_{CF}(r)$, and $g_{CH}(r)$ in the equimolar BH mixture, (c) $G(r, \theta)$ function in the equimolar BH mixture, (d) $G(r, \theta)$ function for θ equal to 0° , 45° , and 90° in the equimolar BH mixture.

departure from the corresponding functions observed in the neat liquid 1,3,5-trifluorobenzene. These observations suggest that the local order existing between the 1,3,5-trifluorobenzene molecules in the BT mixture is not affected by the presence of neighboring benzene molecules. However, let us take note that, as shown in a previous study,²¹ stacked dimers of 1,3,5-trifluorobenzene molecules do exist in the neat liquid for distances around 4 \AA . Interestingly enough, these findings are also observed on the pair correlation functions associated with a pair of benzene-1,3,5-trifluorobenzene molecules. Indeed, these functions are very close to those observed for the pairs of 1,3,5-trifluorobenzene molecules themselves (compare Figures 10 with 9). Therefore it appears that stacked configurations between benzene and 1,3,5-trifluorobenzene molecules are rather favoured at distances ranging between 3.5 and 4.5 \AA in BT mixtures.

2. Hexafluorobenzene-1,3,5-Trifluorobenzene Mixture.

For the equimolar HT mixture (representative of the three simulated concentrations) both functions, $G(r, \theta)$ and $g_{cm}(r)$ associated with the pairs of hexafluorobenzene molecules are similar to those observed in the neat liquid hexafluorobenzene (see Figures 11). Furthermore, the simulated functions for the 1,3,5-trifluorobenzene molecules in the mixture have almost the same dependence in r and θ as those observed in the 1,3,5-trifluorobenzene neat liquid (Figures 12). Finally, the simulated correlation functions associated with unlike pairs are very similar

to the ones associated to a pair of 1,3,5-trifluorobenzene molecules and suggest here also that stacked configurations are favored at short distances (Figures 13).

These observations on the simulated HT mixture show that the local order existing between the hexafluorobenzene molecules themselves, as well as between the 1,3,5-trifluorobenzene molecules has not been practically disturbed upon mixing, while pairs of hexafluorobenzene and 1,3,5-trifluorobenzene molecules in a stacked configuration are favored, as in the BT mixture.

We have also estimated the number of neighbouring molecules n in a spherical shell around a given molecule. For the HT mixture the radius of the shell was fixed at $r = 5.0 \text{\AA}$, a distance encompassing the shoulder observed in the $g_{cm}(r)$ functions associated with the 1,3,5-trifluorobenzene molecules. For the pair of 1,3,5-trifluorobenzene molecules (TT), n was found to be 0.6, while for the pair hexafluorobenzene-1,3,5-trifluorobenzene (HT), a value of 0.5 was obtained. Finally for the pair of hexafluorobenzene molecules (HH) n was found to be close to 0.2. Notice that, in the case of the BT mixture, the value of n for the TT, BT, and BB pairs was found to be 0.5, 0.5, and 0.2, respectively, for a similar cut off distance (i.e., $r = 4.8 \text{\AA}$).

These results indicate that the BT and HT mixtures favor the formation of transient heterodimers (BT or HT) in a stacked configuration quite similar to those observed in pure liquid 1,3,5-trifluorobenzene.

As far as the intermediate range order is concerned ($r \geq 8$ Å) we notice that for the hexafluorobenzene molecules in the HT mixture (Figure 11c) the second shell of neighboring molecules appears less pronounced than the corresponding one in the neat liquid hexafluorobenzene. A similar trend was previously found for the benzene molecules in the BT mixture (Figure 8c). In fact this is mostly due to the influence of 1,3,5-trifluorobenzene molecules which favors the formation of stacked configurations at short range between HT and BT molecules and hence tend to redistribute in a more random way the molecules belonging to the second shell.

3. Benzene–Hexafluorobenzene Mixture. Contrasting with the two previous systems the simulated BH mixture reveals more profound modifications of the local structure. Indeed, the $g_{cm}(r)$ function associated with the BH pair of molecules exhibits a very sharp peak centered about 3.7 Å (Figure 14a) which is the signature of a well defined configuration of molecules in the mixture. Incidentally, we notice that the second shell is well developed and that the translational order get smeared rapidly for distances greater than 9 Å. Furthermore, these features are practically concentration independent (Figure 14a).

A better knowledge of the structure of a BH pair can be obtained using the intermolecular atom-atom correlation functions $g_{CC}(r)$, $g_{CF}(r)$, and $g_{CH}(r)$ associated with a pair of atoms belonging to the benzene and the hexafluorobenzene molecules (Figure 14b). The main peak of all these $g_{ij}(r)$ functions is centered at about 4 Å, which means that when the two partners are close to each other they are almost in a face to face configuration in the mixture. This kind of association between the two unlike species can be characterised with the help of the angular pair correlation function which displays a very sharp peak near $\theta \sim 0^\circ$ and for a separation of about 3.7 Å (Figure 14c). More information is given in Figure 14d, where $G(r, \theta)$ is shown for some relevant configurations of the molecules, namely, the parallel (0°), perpendicular (90°), and intermediate configurations (45°). At short distances ($r \leq 4$ Å), only quasi parallel configurations within the BH pairs of molecules exist in the mixture, while at larger distances both parallel and perpendicular configurations coexist (see the inset in Figure 14d). Indeed two well defined peaks situated at about 7 and 11 Å, respectively, are observed for quasi parallel configurations, whereas peaks located at 6.0, 9.0, and 12.5 Å, respectively, are associated with the quasi perpendicular configurations. Notice that the second shell observed in the $g_{cm}(r)$ function (Figure 14a) is built up from the contributions of parallel, intermediate, and perpendicular configurations of neighboring molecules, but each of them occurs at different intermolecular distances (between 6 and 8 Å). From these details, it is easy to understand the weak amplitude of the long range order in the $g_{cm}(r)$ function beyond the second shell: this is a consequence of the out of phase distribution between parallel and perpendicular configurations.

If we consider now the $g_{cm}(r)$ function associated with like pairs of either benzene (BB) molecules or hexafluorobenzene (HH) molecules we notice that there is a sizeable structural rearrangement in all the concentration range investigated (Figure 15). For an analysis of this rearrangement it is better to use the $G(r, \theta)$ function.

As illustrated in Figure 16, if we consider the intermolecular BB correlation, we notice that for a high concentration in benzene, parallel and perpendicular configurations coexist within the first shell with a slight predominance of the perpendicular ones at short distances, between 5 and 6 Å. This situation is rather different from the one previously reported for the pure

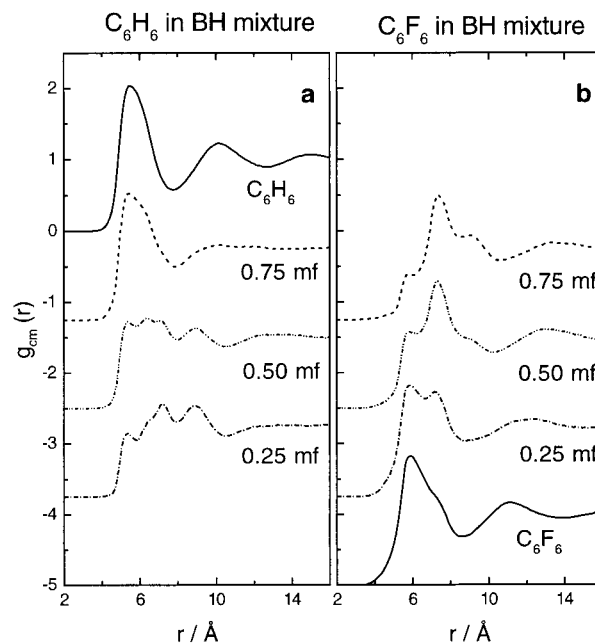


Figure 15. Dependence upon the concentration of the $g_{cm}(r)$ function of the center of mass of a pair of molecules in the benzene–hexafluorobenzene (BH) mixtures at room temperature. (a) For a pair of benzene molecules: (---) 0.25 mf, (---) 0.50 mf, (---) 0.75 mf in benzene, and (—) 1.0 mf (neat liquid benzene). (b) For a pair of hexafluorobenzene molecules: (---) 0.25 mf, (---) 0.50 mf, (---) 0.75 mf, and (—) neat liquid hexafluorobenzene. Curves are shifted from each other (−1.25).

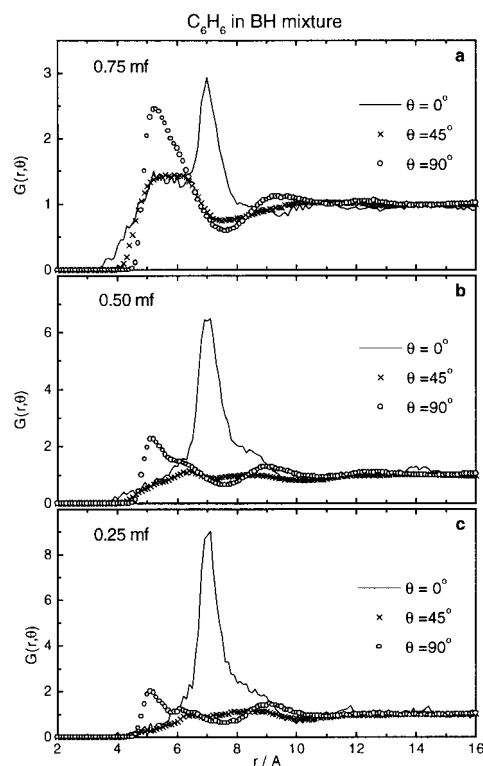


Figure 16. Dependence upon the concentration of the $G(r, \theta)$ function associated with a pair of benzene molecules for θ equal to 0° , 45° , and 90° in the benzene–hexafluorobenzene (BH) mixtures at room temperature: (a) 0.75 mf, (b) 0.50 mf, and (c) 0.25 mf in benzene.

liquid benzene.²⁰ As a matter of fact, a sharp peak at 7 Å, which has no counterpart in the pure liquid benzene is now clearly observed. This peak is assigned to the benzene molecules correlated in a parallel configuration with the other benzene

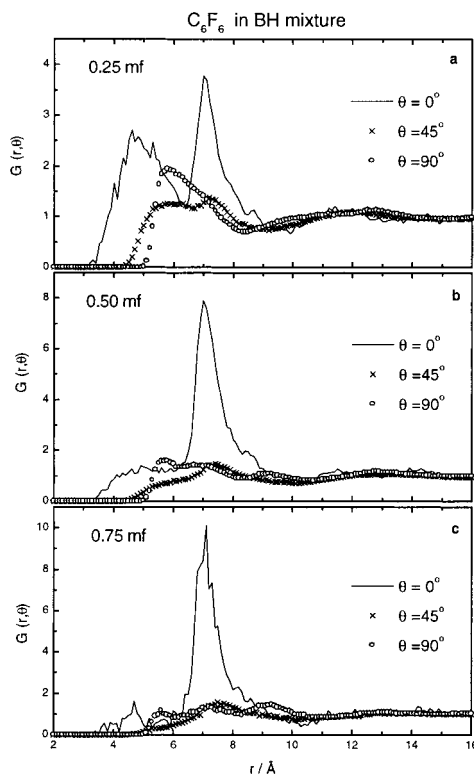


Figure 17. Dependence upon the concentration of the $G(r, \theta)$ function associated with a pair of hexafluorobenzene molecules for θ equal to 0° , 45° , and 90° in the benzene–hexafluorobenzene (BH) mixtures at room temperature: (a) 0.25 mf, (b) 0.50 mf, and (c) 0.75 mf in benzene.

molecules already engaged in the BH heterodimers. On the other hand in the range 4–6 Å the angular distribution is reminiscent of the situation in pure liquid benzene (see Figure 11 of ref 20). Besides, when the concentration in benzene decreases, the relative magnitude of $G(r, \theta)$ in this region (4–6 Å) diminishes as expected (see Figure 16), while the main peak centred at 7 Å ($\theta \sim 0^\circ$) becomes more and more predominant.

Finally, for the HH pair correlations, the same general comments as made above for BB correlations apply as well. However, the main difference comes from the fact that in the first shell parallel and perpendicular configurations are more distributed than previously, a fact already encountered in the hexafluorobenzene neat liquid²⁰ (see Figure 17). Thus, at low concentration in benzene, the relative weight of parallel to perpendicular configurations is similar to the situation in pure liquid C_6F_6 , except a strong enhancement of the peak at 7 Å (see Figure 13 in ref 20 and compare with Figure 17). The latter one is assigned to the C_6F_6 molecules correlated in a parallel way with the other C_6F_6 molecules already engaged in BH heterodimers (stacked structure). When the concentration of benzene molecules increases, the latter peak grows up at the expense of other configurations. This effect and the corresponding one with BB correlations illustrates nicely the structural rearrangement induced by the existence of the BH heterodimers in the mixture.

VII. Conclusion

The structure in the three binary mixtures benzene–1,3,5-trifluorobenzene (BT), benzene–hexafluorobenzene (BH), and hexafluorobenzene–1,3,5-trifluorobenzene (HT) was investigated by neutron diffraction experiment. It is found that the local order is only slightly affected by the temperature variation in the investigated range (298–346 K). In contrast, significant

differences were observed in between these mixtures from the comparison between the experimental data and those deduced from the assumption of ideality in using pure components data. It comes out that the experimental cross section and that calculated for an ideal mixture are rather similar for the BT and the HT mixture as well, whereas a pronounced departure is observed for the BH mixture.

With the help of molecular dynamics simulations based upon model potentials developed for the pure liquids, more information on the structure in these binary mixtures has been obtained. This study has allowed to put in evidence two different classes of systems. First of all, systems which do not exhibit a strong structural enhancement upon mixing, namely, the benzene–1,3,5-trifluorobenzene (BT) and the hexafluorobenzene–1,3,5-trifluorobenzene (HT) mixtures. It is found in that case, that the local order prevailing between molecules of each component in the mixture is not very different from the one which exists in the corresponding neat liquid itself. Moreover, the local structure existing between distinct molecular species in the mixture (i.e., BT or HT) is rather similar to the local order observed in the 1,3,5-trifluorobenzene neat liquid.

The second class of systems, corresponds to mixtures which exhibit a strong structural enhancement upon mixing as the benzene–hexafluorobenzene mixture. In this case, well defined dimers of benzene–hexafluorobenzene molecules in a quasi-stacked configuration, with an average intermolecular distance of about 3.7 Å, are found. In marked contrast with the first class of systems, we find now that the local order existing between the benzene molecules themselves or the hexafluorobenzene molecules in the mixture is very different from the one existing in the corresponding neat liquids. Indeed, it is found now that parallel configurations predominate near 7 Å. A finding which has no counterpart in the corresponding neat liquid and which is associated with a molecule (benzene or hexafluorobenzene) correlated in a parallel configuration with a molecule of the same kind engaged in the stacked structure of an heterodimer.

At this stage several points merit comments. The first one concerns the competition between repulsive, dispersive, and electrostatic forces. In the liquid phase the structure is primarily governed by the short-range, hard repulsive forces of the intermolecular potential as it was pointed out in many studies. But the attractive forces have been recognised to also play a significant role for the local order. For instance, if we consider the benzene and the hexafluorobenzene neat liquids, it is thought that quadrupole–quadrupole interactions play a significant role in the intermolecular rearrangements of the molecules. However, we have shown that in these liquids it is hard to detect on average a preferential orientation between neighboring molecules. Indeed, both parallel and perpendicular configurations are encountered in the first shell and in a quasi random way. In fact this trend can be attributed to the subtle competition between repulsive, dispersive, and electrostatic forces. The situation is better illustrated using as an example liquid 1,3,5-trifluorobenzene where, in contrast to benzene, the quadrupole–quadrupole interactions are negligible in the liquid phase. It comes out, that closest molecules are packed in a stacked configuration leading to the presence of homodimers.

If we consider now the mixtures where 1,3,5-trifluorobenzene liquid is one of the components, we can see that the quadrupole–octopole electrostatic interactions between unlike molecules, do not disturb significantly the local order existing in the neat liquids. Furthermore, the local structure between 1,3,5-trifluorobenzene and benzene (or hexafluorobenzene) molecules

is very similar to the one existing between the 1,3,5-trifluorobenzene molecules in the mixture. Thus, the local order is mainly governed by the short-range intermolecular interactions. Another salient feature results from the fact that parallel configurations between molecules of the same species are enhanced as a consequence of the correlations between unlike molecules.

In binary mixtures, like benzene–hexafluorobenzene, involving molecules with quadrupole moments of opposite sign, we found that the electrostatic interactions enhance the stabilization of the stacked structure which was already favoured by the dispersion forces. However a new finding which cannot be simply deduced on a qualitative ground follows from our analysis. It is found that orientational correlations in the intermediate range order (about 7–11 Å) are governed essentially by the presence of heterodimers. Incidentally, we are close to the point of view expressed by Bartsch et al.¹⁵ which proposed a 1:1 C₆H₆–C₆F₆ complex in a stacked configuration correlated with a molecule belonging to the second co-ordination sphere (7–10 Å) in the mixture. Let us emphasise that this mechanism of interaction could be a key process leading to the liquid–solid phase transition in this mixture.

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