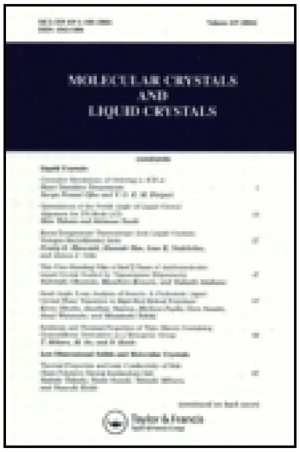

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Influence of the Methyl-group on the Complexation in the Benzenic Family: TheToluene-Hexafluorobenzene System and the p-Xylene-Hexafluorobenzene System

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Influence of the Methyl-group on the Complexation in the Benzenic Family: The Toluene-Hexafluorobenzene System and the *p*-Xylene-Hexafluorobenzene System

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Equilibrium phase diagrams of the toluene-hexafluorobenzene and the *p*-xylene-hexafluorobenzene binary systems are experimentally determined by differential scanning calorimetry and X-ray diffraction analyses. Both diagrams present a complex 1:1 with a rich polymorphism. The optimization of these systems shows the existence of high associated degree in the liquid phase. The comparison of these two systems with the benzene-hexafluorobenzene binary shows that the complex stability increases with number of H-atoms substituted by CH_3-methyl groups in the benzenic ring.

Keywords: Molecular complexes; differential scanning calorimetry; X-ray diffraction; associated liquid model

INTRODUCTION

Organic binary systems are known to give various types of structural alliances, among which molecular alloys and molecular complexes. The

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formation of molecular alloys depends on the degree of isomorphism between the two components: the higher the degree of isomorphism, the greater the tendency to form alloys [1–4]. The formation of complexes depends on the availability of specific attractive interactions such as charge transfer [5] and quadrupole-quadrupole interactions [6].

In our study on the characterization of molecular interactions and on the criterious leading to the complex formation, we have investigated systems involving one highly fluorinated compound which may be enabled to give intermolecular bonds strengthened (by hydrogen bonding character or by charge-transfer).

In this way the two systems presented here are toluene + hexafluorobenzene and paraxylene + hexaflurobenzene. The characteristics of the two systems will be compared with those of the system benzene + hexafluorobenzene. It is shown that the systems have 1:1 complexes with a rich polymorphic nature, which remained unobserved in the exploratory research on the three systems by Duncan and Swinton [7].

PURE COMPONENT DATA

Hexafluorobenzene

The substance was purchased from Aldrich (purity over 99.5%) and was used without further purification. The substance is highly volatile: after mixing with one of the other substances it is necessary to check the composition of the mixed sample. Its temperature and enthalpy of melting are [8] (277.5 ± 0.5) K and (11.20 ± 0.17) kJ/mol. It crystallises in monoclinic symmetry ($P2_1/n$, $Z = 6$) and its cell prameters at 120 K are [9] $a = 16.82$ Å; $b = 9.17$ Å; $c = 5.76$; Å $\beta = 95.80°$.

Toluene

The substance was purchased from Normapur (purity over 99.5%) and was used without further purification. Toluene can be supercooled quite easily, eventually to the vitreous state. It can exist under two different crystalline forms [10]: the stable phase $\alpha (T_{\mathrm{fus}} = 178\,\mathrm{K})$ and the metastable form β under the atmospheric pressure ($T_{\mathrm{fus}} = 157$ K). The form α is monoclinic ($P2_1/c$, $Z = 8$) and the cell parameters at 165 K are [10] $a = 7.666$ Å; $b = 5.832$ Å; $c = 26.980$ Å; $\beta = 105.73°$.

The temperature and the enthalpy of melting of α are [11] 178.15 K and 6.85 kJ/mol.

The *p*-xylene

The substance was purchased from Aldrich (purity over 99%) and used without further purification. Our temperature and enthalpy of melting values are (286.4 ± 0.2) K and (17.3 ± 0.2) kJ/mol. The values from [11] are 286.4 K and 16.8 kJ/mol respectively. It crystallises in monoclinic symmetry ($P2_1/n$, $Z = 2$) and its cell parameters are [12] $a = 5.806$ Å; $b = 5.023$ Å; $c = 11.215$ Å; $\beta = 100.48°$.

PHASE DIAGRAMS

Experimental Procedures

Calorimetric measurements were made with a Perkin-Elmer DSC7 differential scanning calorimeter under the following conditions:

- temperature range between 160 K and 320 K;
- heating and cooling rates of 2 K/min;
- sample mass of 3 to 4 mg;
- n independent measurements for each composition (generally $n = 4$).

All characteristic temperatures, like the liquidus temperatures, were derived from the DSC curves according to the shape factor method [13]. The random errors in the temperatures, as well as those in the heat effects derived from the DSC curves, were obtained by the Student's method with 95% threshold of reliability. The systematic errors are estimated at 0.2 K and 2% in temperatures and heat effects, respectively.

X-ray powder diffraction patterns were made, with an Inel (PS 120) (Cu Kα1 radiation, $\lambda = 1.5406$ Å), in order to compare the spectrum of each complex phases.

The Toluene + Hexafluorobenzene System

Our study of the system revealed that the 1:1 complex gives rise to three different solid forms, hereafter denoted by C_I, C_{II} and C_{III}. The thermodynamic characteristics of the transitions $C_{III} \rightarrow C_{II}$, $C_{II} \rightarrow C_I$ and $C_I \rightarrow$ liquid are given in Table I. The melting temperature of C_I is in good agreement with the value of 283.5 K given by Duncan and Swinton [7].

TABLE I Thermodynamic data of the toluene + hexafluorobenzene system: comparison between experiments and optimization

	Experimental values	*Optimized values*
Complex	$T_{\mathrm{fusC}} = 282.3 \pm 0.9$	$T_{\mathrm{fusC}} = 283.2(1)$
	$\Delta_{\mathrm{fus}}H_{\mathrm{C}} = 14200 \pm 500$	$\Delta_{\mathrm{fus}}H_{\mathrm{C}} = 13880(10)$
		$\Delta_f G^0_C = -16680(9) + 42.4(5)T$
	$T_{\mathrm{trsCIII} \to \mathrm{CII}} = 196 \pm 1$	
	$\Delta_{\mathrm{trs}}H_{\mathrm{C\,III} \to \mathrm{C\,II}} < 50$	
	$T_{\mathrm{trs\ CII} \to \mathrm{CI}} = 241.5 \pm 0.4$	$T_{\mathrm{trsCII} \to \mathrm{CI}} = 241.8(3)$
	$\Delta_{\mathrm{trs}}H_{\mathrm{CII} \to \mathrm{CI}} = 5600 \pm 500$	
Liquid		$H^1_{1,2} = -590(5)$, $S^{(1)}_{1,2} = -1.2(1)$
		$H^2_{1,2} = 42(2)$, $S^2_{1,2} = 0$
		$H^1_{1,3} = 1940(10)$, $S^1_{1,3} = -8.0(5)$
		$H^1_{2,3} = 1940(10)$, $S^1_{2,3} = -8.0(5)$
		$\Delta_{\mathrm{diss}}G^0 = 4300(100)$
Eutectic E_1	$T_{E1} = 177 \pm 1$	$T_{E1} = 178.2(1)$
	degenerate ($x_{E1} < 0.02$)	$x_{E1} \approx 2.4 \times 10^{-3}$
Metatectic M_1	$T_{M1} = 196 \pm 1$	
Metatectic M_2	$T_{M2} = 241.5 \pm 0.4$	$T_{M2} = 241.8(3)$
	$x_{M2} = 0.10 \pm 0.001$	$x_{M2} = 0.10(1)$
Eutectic E_2	$T_{E2} = 263.3 \pm 0.7$	$T_{E2} = 263.5(2)$
	$x_{E2} = 0.80 \pm 0.01$	$x_{E2} = 0.79(1)$
	$\Delta_{\mathrm{fus}}H_{E2} = 9400 \pm 500$	$\Delta_{\mathrm{fus}}H_{E2} = 9700(100)$

The temperatures are in K, the enthalpies in J/mol and the entropies in J/mol/K.

The energy of the $C_{\mathrm{III}} \to C_{\mathrm{II}}$ transition is very weak and the uncertainties in the exploitation of the DSC curves to not allow us to precise the value of $\Delta_{\mathrm{trs}}H_{\mathrm{CIII} \to \mathrm{CII}}$.

The comparison of Inel diffraction patterns of the three phases of the complex (at 160 K, 220 K and 225 K), is shown in Figure 1. The Figure 2 presents the DSC-curve of the complex; we used a rate of 10 K/min in the range of temperature [183 – 213 K] to see clearly the transition $C_{\mathrm{III}} \to C_{\mathrm{II}}$.

The phase diagram of the system is represented by Figure 3 x being the overall mole fraction of C_6F_6. The coordinates of its four three-phase equilibria, as far as they could be precised, are included in Table I.

The *p*-xylene + Hexafluorobenzene System

Our study of the system revealed that the 1:1 complex gives rise to two different solid forms, hereafter denoted by C'_{I} and C'_{II}. The thermodynamics characteristics of the transitions $C'_{\mathrm{II}} \to C'_{\mathrm{I}}$ and $C'_{\mathrm{I}} \to C'_{L}$ are given in

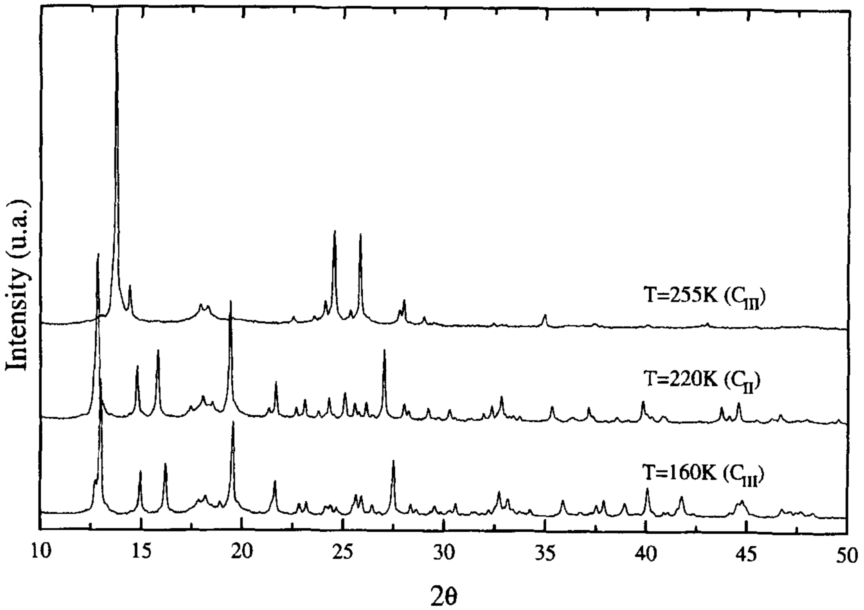

FIGURE 1 Comparison between isothermal diffraction patterns ($T = 225\,K$, $220\,K$ and $160\,K$) of the complex 1:1 in the toluene + hexafluorobenzene system.

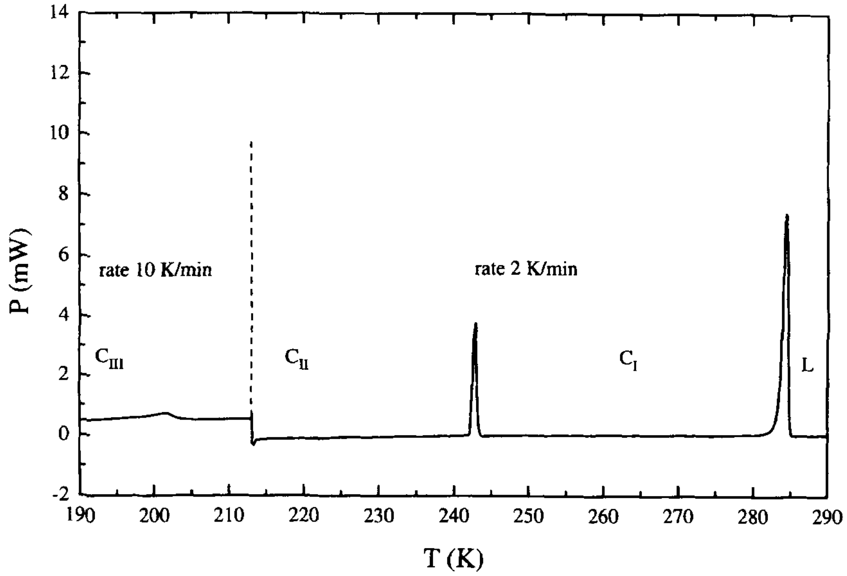

FIGURE 2 DSC curve of the complex 1:1 in the toluene + hexafluorobenzene system.

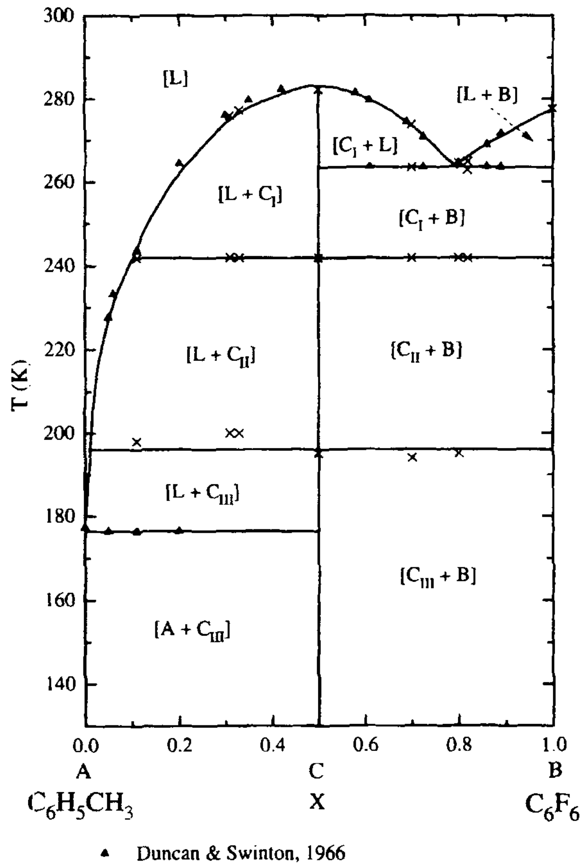

FIGURE 3 Toluene + hexaflurobenzene binary system. The experimental (×, this work; ▲ [7]) and calculated (solid lines) phase diagrams are compared (the optimized parameter values are collected in Tab. I): the liquidus line and the four invariants lead to nine biphasic domains (four solid-solid domains and five solid-liquid domains) and one monophasic liquid domain.

Table II. The temperature of melting of C_I' in good agreement with the value of 300.6 K of Duncan and Swinton [7].

The Figure 4 presents a comparison of the Inel diffraction patterns of each phase of the complex (at 220 K and 225 K). The structure of the phase C_I' was determined by T. Dahl [14]: the phase C_I' crystallizes in the triclinic symmetry ($P_{\bar{1}}$) with cell parameters at 295 K $a = 6.844$ Å; $b = 7.327$ Å; $c = 7.318$ Å; $\alpha = 102.42°$; $\beta = 98{,}13°$; $\gamma = 102.86°$. The Figure 5 shows the DSC-curve of the complex with phase transitions $C_{II}' \to C_I'$ and $C_I' \to C_L'$.

The consistency of the entire experimental data set allows to establish the equilibrium phase diagram (Fig. 6). The coordinates of its three three-phase equilibria are included in the Table II.

TABLE II Thermodynamic data of the *p*-xylene + hexafluorobenzene system: comparison between experiments and optimization

	Experimental values	*Optimized values*
Complex		
	$T_{\text{fusC}'} = 300.5 \pm 0.5$ $\Delta_{\text{fus}} H_{C'} = 23400 \pm 500$	$T_{\text{fusC}'} = 300.5(1)$ $\Delta_{\text{fus}} H_{C'} = 22900(10)$ $\Delta_f G^0_{C'} = -26500(10) + 70.4(8)T$
	$T_{C'II \to C'I} = 229.0 \pm 0.2$ $\Delta_{\text{trs}} H_{C'II \to C'I} = 400$	$T_{C'II \to C'I} = 229.0(1)$ $\Delta_{\text{trs}} H_{C'II \to C'I} = 420$
Liquid		$H^{(1)}_{1,2} = -3120(10)\ S^{(1)}_{1,2} = -7.6(1)$ $H^{(2)}_{1,2} = 190(2)\ S^{(2)}_{1,2} = 0$ $H^{(1)}_{1,3} = 3420(10)\ S^{(1)}_{1,3} = -1.6(1)$ $H^{(1)}_{2,3} = 3420(10)\ S^{(1)}_{2,3} = -1.6(1)$ $\Delta_{\text{diss}} G^0 = 7930(10) - 12.7(8)T$
Eutectic E_1		
	$T_{E1} = 278.5 \pm 0.4$ $x_{E1} = 0.17 \pm 0.01$	$T_{E1} = 278.3(2)$ $x_{E1} = 0.17(1)$
Eutectic E_2		
	$T_{E2} = 269.2 \pm 0.6$ $x_{E2} = 0.86 \pm 0.01$	$T_{E2} = 269.2(2)$ $x_{E2} = 0.86(1)$

The temperatures are in K, the enthalpies in J/mol and the entropies in J/mol/K.

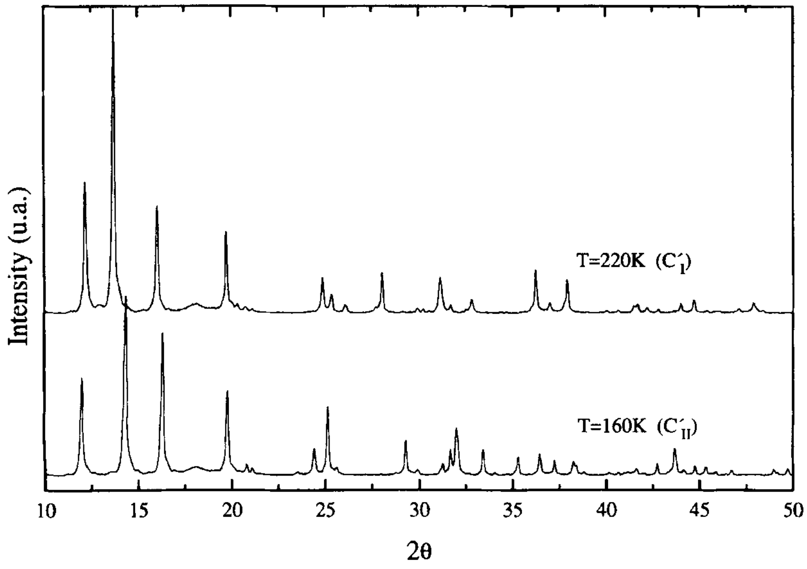

FIGURE 4 Comparison between isothermal diffraction patterns (T = 220 K and 160 K) of the complex 1:1 in the *p*-xylene + hexafluorobenzene system.

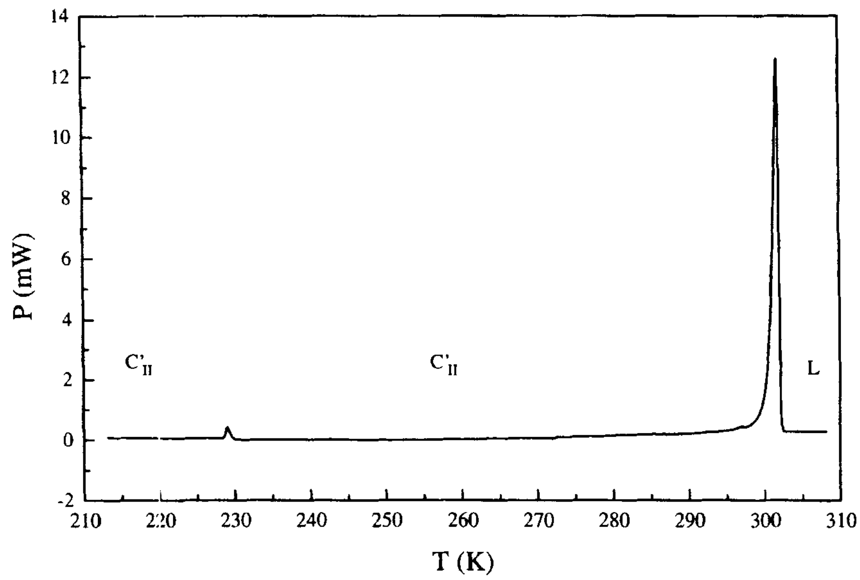

FIGURE 5 DSC curve of the complex (1:1) in the *p*-xylene + hexafluorobenzene system.

THERMODYNAMIC ANALYSIS

In the case of the systems studied all solid phases have fixed compositions. It implies that a thermodynamic mixing model is needed for the liquid state only. An obvious choice is the associated liquid model, which is based on the assumption that the molecular complexes only partly dissociate in the liquid state. In addition, the heat of mixing displayed in Figure 7 for *p*-xylene + hexafluorobenzene [15] has the typical shape in combination with a negative effect found in the case of complex formation.

In the mixing model, interactions are considered between three species. These are *A* (benzene, toluene or *p*-xylene), *B* (hexafluorobenzene) and (*A*:*B*). The Gibbs energy referred to the *A* and *B* species takes the form:

$$\Delta_{\mathrm{mix}}G_L = \left\{ \sum_{i=1}^{2} \sum_{\substack{j=2 \\ j>i}}^{3} x_i x_j [H_{i,j}^{(1)} - TS_{i,j}^{(1)} + (H_{i,j}^{(2)} - TS_{i,j}^{(2)})(x_i - x_j)]/ \right.$$

$$\left. -x_3[\Delta_{\mathrm{diss}}H^0 - T\Delta_{\mathrm{diss}}S^0] + RT \sum_{i=1}^{3} x_i \ln x_i \right\} \Big/ (1 + x_3)$$

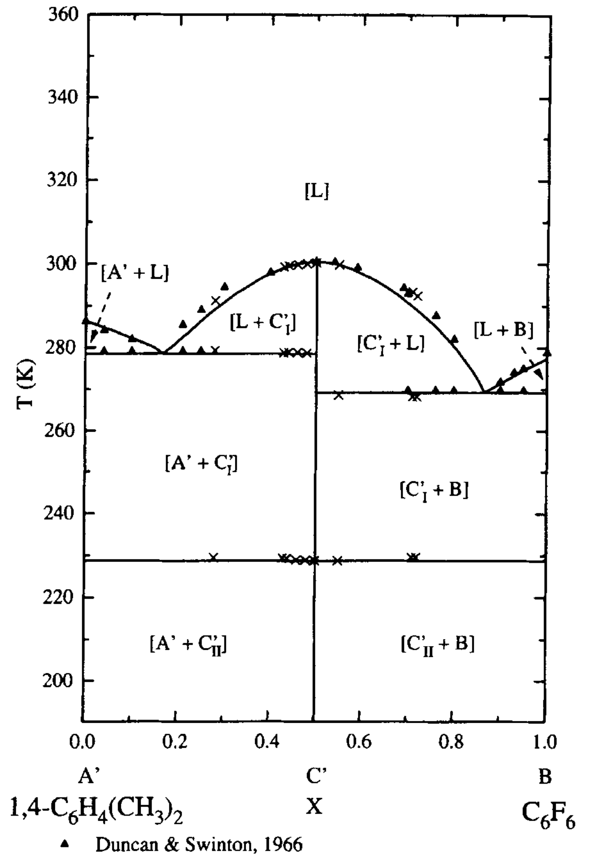

FIGURE 6 *p*-xylene + hexafluorobenzene binary system: comparison between experimental (×, this work; ▲, [7]) and calculated (solid lines) phase diagrams (the optimized values are collected in Tab. II). The eight biphasic domains (four solid-solid domains and four solid-liquid domains) and one monophasic liquid domain are the consequence of the liquidus line and of the three invariants.

where R is the gas constant and x_i the mole fractions of $A\,(i = 1)$, $B\,(i = 2)$ and $(A{:}B)$ $(i = 3)$.

The expression $\Delta_{\mathrm{diss}}H^0 - T\Delta_{\mathrm{diss}}S^0$ represents the standard Gibbs free energy of dissociation of $(A{:}B)$ $\Delta_{\mathrm{diss}}G^0$, referred to the pure liquid components.

In the present work the changes of $\Delta_{\mathrm{diss}}H^0$ and $T\Delta_{\mathrm{diss}}S^0$ and all other heat capacity influences are neglected. In other words it is assumed that all Gibbs energy functions change in a linear manner with temperature.

With the help of the computer program BIMING [16] the phase diagram data can be optimized along with the thermodynamic functions of the

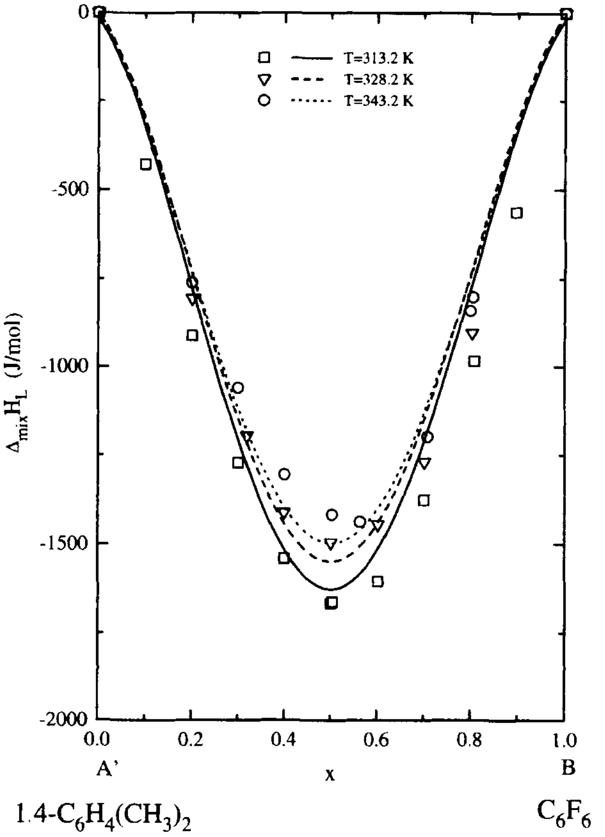

FIGURE 7 *p*-xylene + hexafluorobenzene binary system. The liquid mixing enthalpy data (□, ▽, ○, [15]) are fitted by the parameter set given in Table II.

system. BIMING is an iterative procedure based on the method of minimization by Nelder and Mead [17].

The toluene + hexafluorobenzene System

In the case of this system the following additional approximations have been made. Owing to the small heat effect of the transition between C_{III} and C_{II} the two forms have been described by the same Gibbs energy expression. In view of the fact that the "compound liquidus" is almost perfectly symmetrical with respect to $x = 0.5$, the adjustable parameters $H^{(1)}_{2,3}$ and $S^{(1)}_{2,3}$ were set equal to the parameters $H^{(1)}_{1,3}$ and $S^{(1)}_{1,3}$. In addition $S^{(2)}_{1,2}$, whose contribution is small, was set to zero.

As follows from Table I experimental and optimized values are in good agreement. The solid curve in Figure 3 represent the calculated phase diagram. In Table III a comparison is made between the experimental heat of mixing data of Andrews *et al.* [15] and the calculated values. The computational result corresponds to a rapid decrease with temperature of the associated character in the equimolar liquid mixture: $x_3(283.2\,\mathrm{K}) = 0.63$; $x_3(343.2\,\mathrm{K}) = 0.34$.

The *p*-xylene + hexafluorobenzene System

In the case of this system the same computational procedure was followed as for toluene + hexafluorobenzene system. The results are given in Table II along with the experimental values. The calculated phase diagram is show in Figure 6 together with the experimental data. In Figure 7a comparison is made between the experimental heat of mixing data of Andrews *et al.* [15] and the calculated functions. Again, and according to the computational result, the associated character of the liquid decreases with increasing temperature. For the equimolar liquid mixture we calculated $x_3(300.5\,\mathrm{K}) = 0.37$; $x_3(343.2\,\mathrm{K}) = 0.28$.

The Benzene + hexafluorobenzene System

Owing to the availability of new experimental data concerning its complex C" and for the sake of comparison, we made a new thermodynamic analysis of the system benzene + hexafluorobenzene (see also [8]). The outcome of the analysis is given in Table IV in Figure 8 the calculated phase diagram is presented along with the experimental data.

TABLE III Enthalpy of mixing in the toluene + hexafluorobenzene system: comparison between experiments and calculation

x	$\Delta_{mix}H_{L,\,exp}(J/mol)$*	$\Delta_{mix}H_{L,\,calc}(J/mol)$**
	$T = 283.2\,\mathrm{K}$	
0.5	−1400	−1400
	$T = 313.2\,\mathrm{K}$	
0.4997	−1140	−1030
0.5019	−1150	−1030
	$T = 382.2\,\mathrm{K}$	
0.4976	−910	−890
0.513	−890	−880
	$T = 343.2\,\mathrm{K}$	
0.5002	−650	−800
0.4971	−660	−800

* Calorimetry measurements of Andrews *et al.* [15].

** Calculated values come from the parameter set given in Table I.

TABLE IV Thermodynamic data of the benzene + hexafluorobenzene system: comparison between experiments and optimization

	Experimental values	*Optimized values*
Complex	$T_{\mathrm{fusC''}} = 297.6$ $\Delta_{\mathrm{fus}}H_{\mathrm{C''}} = 20500 \pm 280$ $T_{\mathrm{trs}}H_{\mathrm{C''II} \to \mathrm{C''I}} = 273.7 \pm 0.5$ $\Delta_{\mathrm{trs}}H_{\mathrm{C''II} \to \mathrm{C''I}} = 950 \pm 50$ $T_{\mathrm{trsC''III} \to \mathrm{C''II}} = 249.2 \pm 0.7$ $\Delta_{\mathrm{trs}}H_{\mathrm{C''III} \to \mathrm{C''II}} = 600$ $T_{\mathrm{trsC''IV} \to \mathrm{C''III}} = 199$ $\Delta_{\mathrm{trs}}H_{\mathrm{C''IV} \to \mathrm{C''III}} < 200$	$T_{\mathrm{fusC''}} = 2972.(2)$ $\Delta_{\mathrm{fus}}H_{\mathrm{C''}} = 20200(500)$ $\Delta_f G^0_{\mathrm{C''}} = -21120(20) + 57.3(5)T$ $T_{\mathrm{trs\ C''II} \to \mathrm{C''I}} = 273.7(1)$
Liquid		$H^{(1)}_{1,2} = -760(5)\ S^{(1)}_{1,2} = -3.2(1)$ $H^{(2)}_{1,2} = 1095(2)\ S^{(1)}_{1,2} = 3.4(1)$ $H^{(1)}_{1,3} = 4870(10)\ S^{(1)}_{1,3} = -3.5(5)$ $H^{(1)}_{2,3} = 1950(10)\ S^{(1)}_{2,3} = -5.3(5)$ $\Delta_{\mathrm{diss}}G^0 = 5080(10) - 9.4(8)\ T$
Eutetic *E*1	$T_{E1} = 270.9$ $x_{E1} = 0.12$ $\Delta_{\mathrm{fus}}H_{E1} = 9700 \pm 110$	$T_{E1} = 269.8(5)$ $x_{E1} = 0.122(6)$ $\Delta_{\mathrm{fus}}H_{E1} = 10190(10)$
Eutectic *E*2	$T_{E2} = 268.8$ $x_{E2} = 0.85$ $\Delta_{\mathrm{fus}}H_{E2} = 10630 \pm 110$	$T_{E_2} = 268.6(1)$ $x_{E2} = 0.849(6)$ $\Delta_{\mathrm{fus}}H_{E2} = 10850(5)$
Metatectic *M*	$T_M = 273.7 \pm 0.5$ $x_M = 0.14$	$T_M = 273.7$ $x_M = 0.15(1)$
Metatectic *M*'	$T_M = 273.5 \pm 0.5$ $x_{M'} = 0.83$	$T_M = 273.7$ $x_{M'} = 0.83(1)$

The temperatures are in K, the enthalpies in J/mol and the entropies in J/mol/K.

DISCUSSION

In Table V the output of the optimization of the three systems is represented as far as the evidence of complex formation is concerned. In order to allow a comparison of the three systems, the information in the table is brought to the uniform temperature of 313.2 K. First of all one can observe that the stability of C and C' are greater than the stability of C" and so in the liquid as well as in the solid state. The interaction between substituted fluorine and substituted methyl seems to be more attractive than the interaction between fluorine and hydrogen. The question whether the extra attraction is proportional to the number of substituted methyl groups is not so easy to

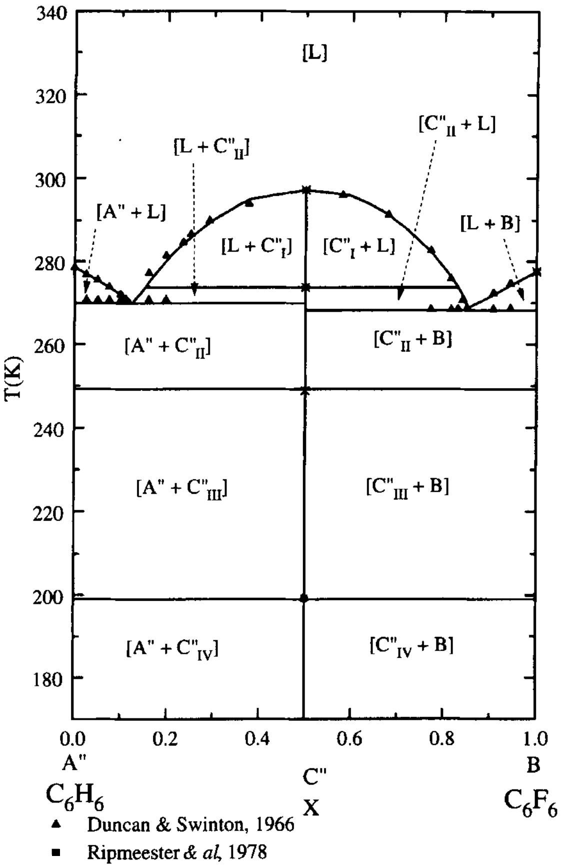

FIGURE 8 Benzene + hexafluorobenzene binary system. The experimental phase diagram (×, this work; ▲, [7]; ■, [18]) is fitted by the parameter set given in Table IV.

answer. Not only that only part of the information in Table V does suggest so, there is also the fact that the molecules of benzene, toluene, *p*-xylene have different symmetries.

In this work, we have given evidence, for the first time, of the rich polymorphism nature of the complexes C and C'. Three diffrent forms are found C and two for C'. The highly polymorphic nature of C" (four different forms) is possibly explained by the easiness with which the benzene molecule is able to turn in its plane [18–21]. The methyl-group in the toluene and in the *p*-xylene does not allow the rotation and, therefore, it should explain the weaker solid phases number of C and C'.

TABLE V Stability of the complexes: comparison between liquid and solid state

System with	*Number of methyl-group*	$\Delta_f G^0$* *(J/mol)*	$\Delta_{mix} H_L(x = 0.5)$ *(J/mol)**	$x_3(x = 0.5)$	$\Delta_{diss} G^0(x = 0.5)$ *(J/mol)**	$\Delta_{xs} C_L^p(x = 0.5)$ *(J/mol/K)***
benzene	0	– 3270(30)	– 410(50)	0.16(1)	2300(200)	1.8 ± 0.3
toluene	1	– 3530(30)	– 1030(20)	0.45(1)	4300(100)	16.7 ± 0.3
p-xylene	2	– 4580(50)	– 1690(10)	0.34(1)	4000(250)	12.3 ± 0.3

All these data are given at $T = 313.2$ K.

* Optimized values.

** Experimental values of Andrews *et al.* [15].

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