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Crystal Structures and Thermochemical Properties of *n*-Nonylammonium Dihydrogen Phosphate $C_9H_{19}NH_3\cdot H_2PO_4(s)$ and *n*-Octylammonium Dihydrogen Phosphate $C_8H_{17}NH_3\cdot H_2PO_4(s)$

Li-Jun Zhang,[†] Zhi-Cheng Tan,[‡] Jing-Tao Chen,[§] and You-Ying Di*,[†]

[†]Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, College of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, Shandong Province, P. R. China

[‡]China Ionic Liquid Laboratory and Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

[§]Department of Chemistry, Shanxi Educational College, Xi'an 710061, P. R. China

ABSTRACT: The crystal structures of *n*-nonylammonium dihydrogen phosphate and *n*-octylammonium dihydrogen phosphate were determined by X-ray crystallography. Lattice potential energies of the compounds were obtained from the crystallographic data. The molar enthalpies of dissolution of the two compounds at various molalities in the double-distilled water were measured at $T = 298.15$ K by means of an isoperibol solution-reaction calorimeter, respectively. According to the Pitzer's electrolyte solution theory, the standard molar enthalpies of dissolution of the two compounds at infinite dilution were determined to be 34.50 $kJ\cdot mol^{-1}$ and 22.32 $kJ\cdot mol^{-1}$, and the Pitzer's parameters $\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$ were obtained. The values of apparent relative molar enthalpies ($^{\Phi}L$) of the title compounds and relative partial molar enthalpies ($\bar{L}_2$ and $\bar{L}_1$ of the solute and the solvent at different concentrations were derived from the experimental values of the enthalpies of dissolution of the two compounds.

INTRODUCTION

The long chain alkyl hydrocarbons and their derivatives can be used as phase change materials for thermal energy storage due to high enthalpies of solid−solid phase transitions. Recently, microencapsulated *n*-eicosane,[1] nano-encapsulated *n*-tetradecane, and *n*-nonadecane are reported as phase transition materials for thermal energy storage. In addition, some complexes, $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4(s)$ (where M is a divalent metal atom), are carefully investigated.[2,3] Alkyl dihydrogen phosphate is an important intermediate in organic synthesis. In recent years, great attention has been paid to the phase transition behavior of alkyl dihydrogen phosphate. However, the lattice potential energies and some important thermodynamic properties of the title compounds have not been found in the literature, which restricts the progress of relevant theoretical studies and application development of the title compounds. For these purposes, in the present work, crystal structures of the title compounds are determined by X-ray crystallography, and the enthalpies of dissolution of the title compounds in the water are measured by an isoperibol solution-reaction calorimeter. Lattice potential energies and molar enthalpies of dissolution of the title compounds at infinite dilution are obtained based on the crystal structures and experimental enthalpies of dissolution at different concentrations.

EXPERIMENTAL SECTION

Synthesis and Characterization of the Compounds. *n*-Nonylamine (0.98 in mass fraction), *n*-octylamine (0.99 in mass fraction), and phosphoric acid (0.98 in mass fraction) chosen as the reactants and anhydrous ethyl alcohol used as the solvent are of analytical grade. *n*-Nonylamine is accurately weighed at the molar ratio of $n[CH_3(CH_2)_8NH_2]/n(H_3PO_4) = 1{:}1$. About 35 mmol of *n*-nonylamine is first dissolved in a 100 cm^3 flask with a certain amount of anhydrous ethanol, and then phosphoric acid (about 35 mmol) is added slowly. The white precipitation is produced at once. The mixture is heated and stirred under reflux for 4 h. The final solution is naturally cooled to room temperature and filtered, and the white product is washed by anhydrous ethanol three times. The white solid is recrystallized using deionized water, and colorless crystals are prepared by natural evaporation of a solution of the title compound in deionized water at room temperature. Finally, the sample is placed in a vacuum desiccator at 298.15 K to dry in vacuum for 6 h. *n*-Octylammonium dihydrogen phosphate is synthesized in the same manner as *n*-nonylammonium dihydrogen phosphate. The actual mass fraction purities of the two compounds are determined to be >0.995 by a chromatographic method (high-performance liquid chromatography, HPLC). We have used an HPLC method with a differential refraction detector for the measurement of the compounds, and the method of area normalization is available for analyzing the purity of the compounds. The compounds are measured respectively three times. We take the average value of the results. We have verified from the experiments that the HPLC pattern of each of the two samples only has one component (single peak). The phosphate contents of the

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compounds are determined by chemical analysis. Elemental analysis (C, H, and N) is carried out on a Vario EL III CHNOS instrument made in Germany. Anal. Calc. for $C_9H_{19}NH_3 \cdot H_2PO_4$: C, 0.4480; H, 0.1003; N, 0.0581. Found: C, 0.4482; H, 0.1004; N, 0.0580. This shows that the purity of the sample prepared is higher than 0.995 in mass fraction. The other melting point is (123 to 124) °C. Anal. Calc. for $C_8H_{17}NH_3 \cdot H_2PO_4$: C, 0.4229; H, 0.0976; N, 0.0616. Found: C, 0.4230; H, 0.0975; N, 0.0617. This shows that the purity of the sample prepared is higher than 0.996 in mass fraction.

X-ray Crystallography. A single crystal suitable for X-ray analysis is glued to a fine glass fiber and then mounted on the Bruker Smart-1000 CCD diffractometer with Mo Kα radiation, λ = 0.071073 nm. The intensity data are collected at $T = (298 \pm 2)$ K. The structure is solved by direct methods and expanded using Fourier techniques with the SHELXL-97 program.[4] The non-hydrogen atoms are refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms are added theoretically, riding on the concerned atoms and not refined. Crystal data and refinement details are summarized in Table 1.

Isoperibol Solution-Reaction Calorimetry. The isoperibol solution-reaction calorimeter consists primarily of a precision temperature control system, an electric energy calibration system, a calorimetric body, an electric stirring system, a thermostatic bath made from transparent silicate glass, a precision temperature measuring system, and a data acquisition system. The principle and structure of the calorimeter are described in detail elsewhere.[5]

The reliability of the calorimeter is verified previously[5] by measuring the dissolution enthalpy of KCl (calorimetrically primary standard) in the double-distilled water at T = 298.15 K. The mean dissolution enthalpy is $(17\,547 \pm 13.0)$ J·mol^{-1} for KCl, which compares with the corresponding published data, $(17\,536 \pm 3.4)$ J·mol^{-1};[6] the uncertainty is ± 0.30 %.

In all dissolution experiments, the double-distilled water is chosen as the calorimetric solvent for measuring the dissolution enthalpies of *n*-nonylammonium dihydrogen phosphate and *n*-octylammonium dihydrogen phosphate, respectively.

RESULTS AND DISCUSSION

Crystal Structures. The X-ray single crystal diffraction technique shows one of the title compounds to be *n*-nonylammonium dihydrogen phosphate. The molecular structure of $C_9H_{19}NH_3 \cdot H_2PO_4$(s) is shown in Figure 1. Crystal data and refinement details are summarized in Table 1. The selected bond

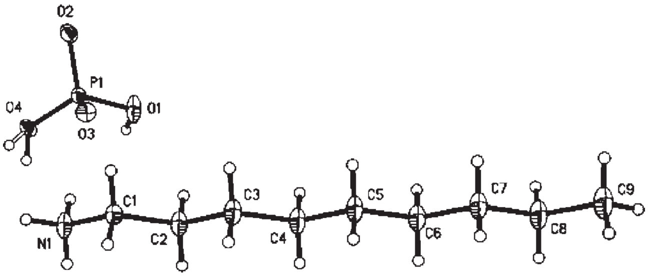

Figure 1. Molecular structure of *n*-nonylammonium dihydrogen phosphate.

Table 1. Crystallographic Data and Structure Refinement for the Title Compounds

crystallographic data	structure refinement	
empirical formula	$C_8H_{17}NH_3 \cdot H_2PO_4$	$C_9H_{19}NH_3 \cdot H_2PO_4$
formula weight	0.22724 kg·mol^{-1}	0.24127 kg·mol^{-1}
temperature	298(2) K	298(2) K
wavelength	0.071073 nm	0.71073 nm
crystal system	orthorhombic	orthorhombic
space group	*Pbcn*	*Ama*2
unit cell dimensions	a = 0.73810(8) nm	a = 0.73571(8) nm
	b = 0.91761(10) nm	b = 3.7300(3) nm
	c = 3.4770(3) nm	c = 0.46070(5) nm
	$\alpha = 90°, \beta = 90°, \gamma = 90°$	$\alpha = 90°, \beta = 90°, \gamma = 90°$
volume	2.3549(4) nm^3	1.2643(2) nm^3
Z	8	4
calculated density	1.282 mg·m^{-3}	1.268 mg·m^{-3}
absorption coefficient	0.226 mm^{-1}	0.215 mm^{-1}
F(000)	992	528
crystal size	0.39 × 0.18 × 0.11 mm	0.49 × 0.25 × 0.15 mm
θ range for data collection	2.34° to 25.02°	2.18° to 25.02°
limiting indices	$-4 \le h \le 8, -10 \le k \le 10, -41 \le l \le 40$	$-8 \le h \le 5, -43 \le k \le 44, -5 \le l \le 5$
reflections collected/unique	8761/2061 [R(int) = 0.1284]	3092/685 [R(int) = 0.0707]
completeness to θ = 25.02	99.3 %	98.6 %
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	2061/0/129	685/1/100
goodness-of-fit on F^2	1.021	0.981
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0809$, $wR_2 = 0.1742$	$R_1 = 0.0435$, $wR_2 = 0.1011$
R indices (all data)	$R_1 = 0.1405$, $wR_2 = 0.2110$	$R_1 = 0.0537$, $wR_2 = 0.1096$
largest diff. peak and hole	(337 and −626) e·nm^{-3}	(263 and −343) e·nm^{-3}

lengths and angles of the title compound are listed in Table 2. The hydrogen bonds are given in Table 3. It is found from Table 1 that the crystal system of *n*-nonylammonium dihydrogen phosphate is orthorhombic, the space group is *Ama*2, and unit cell dimensions are a = 0.7357(8) nm, b = 3.7300(3) nm, and c = 0.4607(5) nm; α = 90°, β = 90°, γ = 90°, and Z = 4. The values of the density and volume are important for the calculation of lattice energy of the compound. In comparison with the literature, the crystal system of the compound reported in the literature[7] is monoclinic, and the space group is $P2_1/n$. This shows that the substances reported in the literature and described in the article belong to two different crystals in isomorphism.

The X-ray single crystal diffraction technique shows the other compound to be *n*-octylammonium dihydrogen phosphate. The molecular structure of $C_8H_{17}NH_3 \cdot H_2PO_4(s)$ is shown in Figure 2. Crystal data and refinement details are summarized in Table 1. The selected bond lengths and angles of the title compound are listed in Table 4. The hydrogen bonds are given in Table 5. Unit cell parameters are a = 0.73810(8) nm, b = 0.91761(10) nm, and c = 3.4770(3) nm; α = 90°, β = 90°, and γ = 90°, respectively. The crystal structure of the compound is orthorhombic, and the space group is *Pbcn*, as shown in Table 1. It can be seen that the crystal data and the structure of *n*-octylammonium dihydrogen phosphate determined in this paper almost agree with those of the literature.[8] The crystal structure of the compound reported in the literature[8] is monoclinic, and the space group is $P2_1/c$. The structure of the title compound has a higher degree of symmetry than that reported. That is because the substance can display the polytypism in different surroundings.

The two compounds are composed of the regular alternation of inorganic and hydrocarbon regions through hydrogen bonding, as shown in Figures 3 and 4. The packing of structures of the title compounds is a "sandwich" system formed by hydrogen bonds (N−H···O); that is, each inorganic layer is sandwiched between alkylammonium layers, as seen in Figures 3 and 4. The compounds crystallized in the form of layers of PO_4 tetrahedron are linked by hydrogen bonds alternating with layers of alkylammonium. Weak van der Waals forces act between the alkyl chains. In addition, it is found that the action of hydrogen bonds is very strong, as shown in Tables 3 and 5. The results indicate that the hydrogen bonds play an important role in stabilizing the

Table 2. Bond Lengths (nm) and Angles (deg) for $C_9H_{19}NH_3 \cdot H_2PO_4(s)$

bonds	bond lengths	bonds	bond angles
P(1)−O(1)	0.1552(4)	O(3)−P(1)−O(2)	114.8(3)
P(1)−O(2)	0.1500(4)	O(3)−P(1)−O(1)	109.4(2)
P(1)−O(3)	0.1504(5)	O(2)−P(1)−O(1)	104.72(19)
P(1)−O(4)	0.1554(4)	O(3)−P(1)−O(4)	110.7(3)
N(1)−H(1A)	0.089	O(2)−P(1)−O(4)	107.4(2)
N(1)−C(1)	0.1473(6)	O(1)−P(1)−O(4)	109.6(3)
C(1)−C(2)	0.1510(6)	N(1)−C(1)−C(2)	112.2(4)
C(2)−C(3)	0.1517(7)	C(1)−C(2)−C(3)	111.2(5)
C(3)−C(4)	0.1518(7)	C(2)−C(3)−C(4)	113.9(5)
C(4)−C(5)	0.1514(7)	C(5)−C(4)−C(3)	113.9(6)
C(5)−C(6)	0.1514(8)	C(4)−C(5)−C(6)	114.0(6)
C(6)−C(7)	0.1531(9)	C(5)−C(6)−C(7)	113.7(7)
C(7)−C(8)	0.1515(9)	C(8)−C(7)−C(6)	113.3(7)
C(8)−C(9)	0.1524(10)	C(7)−C(8)−C(9)	113.1(9)

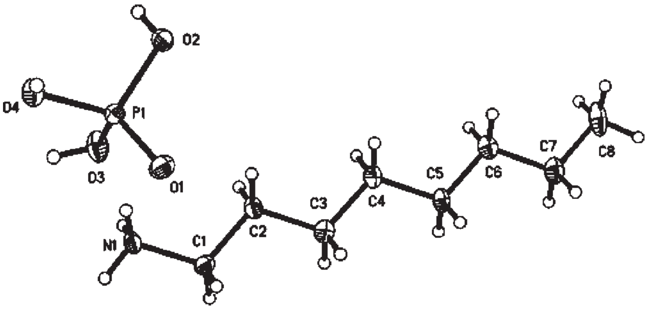

Figure 2. Molecular structure of *n*-octylammonium dihydrogen phosphate.

Table 4. Bond Lengths (nm) and Angles (deg) for $C_8H_{17}NH_3 \cdot H_2PO_4$ (s)

bonds	bond lengths	bonds	bond angles
N(1)−C(1)	0.1474(6)	O(1)−P(1)−O(3)	113.9(2)
O(1)−P(1)	0.1492(4)	O(1)−P(1)−O(4)	111.8(2)
O(2)−P(1)	0.1568(4)	O(3)−P(1)−O(4)	106.3(2)
O(3)−P(1)	0.1533(4)	O(1)−P(1)−O(2)	107.4(2)
O(4)−P(1)	0.1546(4)	O(3)−P(1)−O(2)	108.2(2)
C(1)−C(2)	0.1512(7)	O(4)−P(1)−O(2)	109.1(2)
C(2)−C(3)	0.1512(7)	N(1)−C(1)−C(2)	112.8(4)
C(3)−C(4)	0.1522(7)	C(3)−C(2)−C(1)	112.8(5)
C(4)−C(5)	0.1513(7)	C(2)−C(3)−C(4)	114.5(5)
C(5)−C(6)	0.1519(7)	C(5)−C(4)−C(3)	114.4(5)
C(6)−C(7)	0.1517(7)	C(4)−C(5)−C(6)	114.8(5)
C(7)−C(8)	0.1520(8)	C(7)−C(6)−C(5)	114.9(5)
N(1)−H(1A)	0.08900	C(6)−C(7)−C(8)	114.7(6)

Table 3. Hydrogen Bonds (nm and deg) for $C_9H_{19}NH_3 \cdot H_2PO_4$ (s)

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)	symmetry code
N(1)−H(1A)···O(4)#2	0.089	0.193	0.2769(6)	157.6	$-x + 1, -y + 1, z + 1$
N(1)−H(1A)···O(4)#3	0.089	0.193	0.2769(6)	157.6	$x - 1/2, -y + 1, z + 1$
N(1)−H(1B)···O(2)#1	0.089	0.198	0.2856(6)	166.6	$-x + 3/2, y, z$
N(1)−H(1B)···O(2)#1	0.089	0.216	0.2979(5)	152.7	
O(1)−H(1C)···O(3)#4	0.082	0.177	0.2580(7)	169.6	$x, y, z - 1$
O(1)−H(1C)···O(3)#5	0.082	0.201	0.2580(7)	125.8	$-x + 3/2, y, z - 1$
O(4)−H(4A)···O(4)#6	0.082	0.174	0.2550(7)	169.0	$-x + 1, -y + 1, z$
O(4)−H(4B)···O(2)#7	0.082	0.155	0.2316(6)	153.8	$x - 1/2, -y + 1, z$
O(4)−H(4B)···O(2)#7	0.082	0.155	0.3216(6)	153.8	$x - 1/2, -y + 1, z$
O(4)−H(4A)···O(4)#6	0.082	0.174	0.2550(7)	169.0	$-x + 1, -y + 1, z$

Table 5. Hydrogen Bonds (nm and deg) for $C_8H_{17}NH_3 \cdot H_2PO_4$ (s)

D−H···A	d(D−H)	d(H···A)	d(D···A)	<(DHA)	symmetry code
N(1)−H(1A)···O(3)	0.0890	0.2100	0.2973(6)	168.00	
N(1)−H(1B)···O(4)	0.0890	0.1970	0.2810(6)	156.30	$x + 1/2, y + 1/2, -z + 1/2$
N(1)−H(1C)···O(1)	0.0890	0.1980	0.2836(6)	160.70	$x + 1, y, z$
O(2)−H(2)···O(1)	0.0820	0.1810	0.2612(5)	166.20	$-x + 1/2, y - 1/2, z$
O(3)−H(3)···O(3)	0.0820	0.1740	0.2555(7)	169.30	$-x + 1, y, -z + 1/2$
O(4)−H(4)···O(4)	0.0820	0.1730	0.2544(7)	169.80	$-x, y, -z + 1/2$

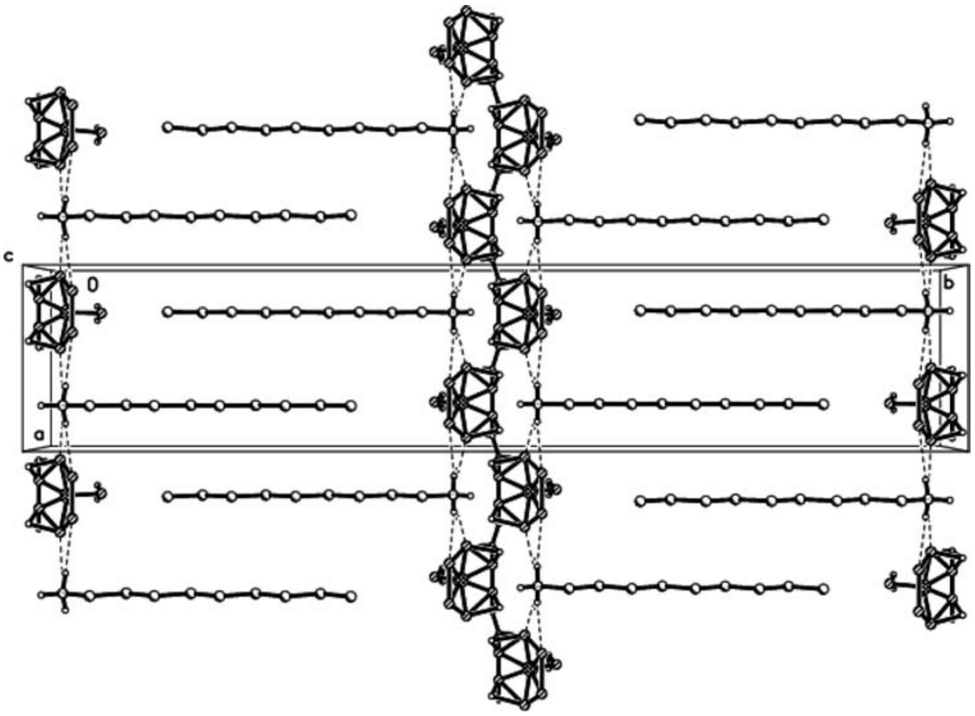

Figure 3. Packing diagram of the compound $C_9H_{19}NH_3 \cdot H_2PO_4$(s).

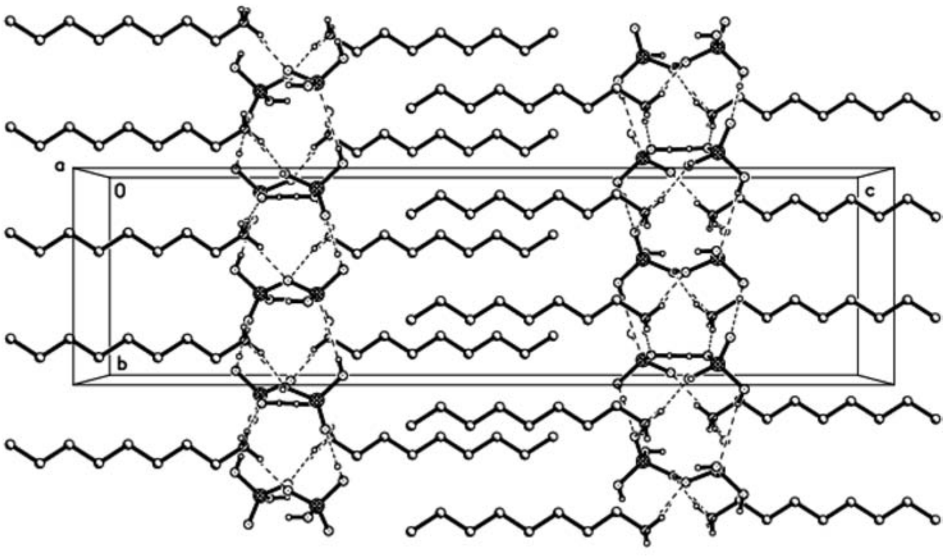

Figure 4. Packing diagram of the compound $C_8H_{17}NH_3 \cdot H_2PO_4$(s).

whole structure of the compound. It can be concluded from the structures of *n*-nonylammonium dihydrogen phosphate and *n*-octylammonium dihydrogen phosphate determined in the paper that a spatial configuration based on the ordered packing of alkylammonium chains can be derived. In the structures of the title compounds, the alkylammonium chains are connected to the dihydrogen phosphates in a similar way. The localization of the N atoms makes the environment of the N atoms and the following two C atoms similar in the title compounds, independent of the parity of atoms in an alkylammonium chain. It follows from this similarity that the localization of the N atoms is governed by the hydrogen bonds between alkylammonium groups and dihydrogen phosphates, which is much stronger than the van der Waals force. The latter interaction force decides the mutual positions of the alkylammonium molecules.

Lattice Potential Energy. The eq 1 used to estimate lattice potential energy of general type of salts M_pX_q is obtained from the literature.[9]

$$U_{\mathrm{POT}} = \sum n_i z_i^{\,2}(\alpha'/V_{\mathrm{m}}^{\,1/3} + \beta') \tag{1}$$

where α' and β' are appropriate fitted coefficients chosen according to the stoichiometry of the salt, n_i is the number of ions with a charge z_i in the formula unit, and V_{m} is the molecular volume.

For the salts MX (1:1), MX_2 (1:2), and M_2X (2:1), eq 1 is changed to:

$$U_{\mathrm{POT}} = |z_+||z_-|\nu(\alpha'/V_{\mathrm{m}}^{1/3} + \beta') \tag{2}$$

where z_+ and z_- are the respective charges on the cation and anion of the compound, and ν is the number of ions per molecule and equals $(p + q)$. In the case of the salts of formula MX with charge ratio (1:1) like *n*-nonylammonium dihydrogen phosphate and *n*-octylammonium dihydrogen phosphate, $z_+ = 1$, $z_- = 1$, $p = 1$, $q = 1$, $\nu = 2$, $\alpha' = 117.3\ \mathrm{kJ \cdot mol^{-1} \cdot nm}$, $\beta' = 51.9\ \mathrm{kJ \cdot mol^{-1}}$, and V_{m} is in units of nm^3,[9]

$$V_{\mathrm{m}} = V_{\mathrm{o}}/Z \tag{3}$$

V_{o} is the unit cell volume, and Z is the number of molecules inside the crystal cell, which are listed in Table 1. The lattice potential energies of *n*-nonylammonium dihydrogen phosphate and *n*-octylammonium dihydrogen phosphate are calculated to be 448.26 $\mathrm{kJ \cdot mol^{-1}}$ and 456.49 $\mathrm{kJ \cdot mol^{-1}}$, respectively. As we all know, the bigger the value of lattice potential energy, the higher the stability of the compound. Therefore, it is seen from the data that *n*-octylammonium dihydrogen phosphate is more stable than *n*-nonylammonium ethylenediamine dihydrochloride.

Enthalpies of Dissolution and Pitzer's Theory. The molar enthalpy of dissolution of the compound ($\Delta_s H_{\mathrm{m}}$) in water is expressed as:[10]

$$\Delta_s H_{\mathrm{m}} = \Delta_s H_{\mathrm{m}}^{\infty} + {}^{\Phi}L \tag{4}$$

in which $\Delta_s H_{\mathrm{m}}^{\infty}$ is the molar enthalpy of dissolution at infinite dilution and ${}^{\Phi}L$ is the apparent relative molar enthalpy.

According to Pitzer's theory, the apparent relative molar enthalpy ${}^{\Phi}L$ may be expressed as:[10]

$$\begin{aligned} {}^{\Phi}L = {} & 2\left(\frac{A_{\mathrm{H}}}{2.4}\right)\ln(1 + 1.2I^{1/2}) \\ & - 2RT^2\left(m\beta_{\mathrm{MX}}^{(0)L} + my'\beta_{\mathrm{MX}}^{(1)L} + \frac{m^2 C_{\mathrm{MX}}^{\Phi L}}{2}\right) \end{aligned} \tag{5}$$

where I is ionic strength, $\beta_{\mathrm{MX}}^{(0)L}$, $\beta_{\mathrm{MX}}^{(1)L}$, and $C_{\mathrm{MX}}^{\Phi L}$ are Pitzer's parameters for enthalpies, the coefficients $\beta_{\mathrm{MX}}^{(0)L}$ and $\beta_{\mathrm{MX}}^{(1)L}$ account for various types of short-range interactions between M and X, and for indirect forces arising from the solvent; the third coefficient $C_{\mathrm{MX}}^{\Phi L}$ is for triple ion interactions and is important only at high concentrations, and $C_{\mathrm{MX}}^{\Phi L}$ may be overlooked because the molality of the sample in dissolution experiment is relatively low. A_{H} is the Debye–Huckel parameter for enthalpy, 1986 $\mathrm{J \cdot mol^{-1}}$ at 298.15 K,[10] and R is the molar gas constant, 8.3145 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$.

The title compounds are easily dissolved in the distilled water at 298.15 K. The molar enthalpies of dissolution of the

Table 6. Values of Molar Enthalpies of Dissolution of $C_9H_{19}NH_3 \cdot H_2PO_4$ (s) at Various Molalities at T = 298.15 K

$10^3\ m$ / $\mathrm{mol \cdot kg^{-1}}$	$\Delta_s H_{\mathrm{m}}$ / $\mathrm{kJ \cdot mol^{-1}}$	${}^{\Phi}L$ / $\mathrm{kJ \cdot mol^{-1}}$	$10^5\ (\partial^{\Phi}L/\partial m)_{T,P}$	$\bar{L}_1$ / $\mathrm{J \cdot mol^{-1}}$	$\bar{L}_2$ / $\mathrm{J \cdot mol^{-1}}$
0.829	32.987 ± 0.054	−1.513 ± 0.054	−17.333 ± 0.065	21.463 ± 0.057	−2.951 ± 0.058
1.250	32.245 ± 0.044	−2.255 ± 0.044	−15.269 ± 0.035	42.736 ± 0.096	−4.159 ± 0.049
1.670	31.553 ± 0.043	−2.947 ± 0.043	−13.514 ± 0.026	67.860 ± 0.099	−5.204 ± 0.048
2.100	30.851 ± 0.055	−3.649 ± 0.055	−11.953 ± 0.026	94.988 ± 0.105	−6.160 ± 0.059
2.490	30.360 ± 0.033	−4.140 ± 0.033	−10.696 ± 0.013	119.023 ± 0.103	−6.799 ± 0.045
2.920	29.892 ± 0.056	−4.608 ± 0.056	−9.409 ± 0.019	144.139 ± 0.123	−7.353 ± 0.060
3.730	29.345 ± 0.028	−5.155 ± 0.028	−7.230 ± 0.008	181.384 ± 0.151	−7.854 ± 0.031
4.470	28.972 ± 0.045	−5.528 ± 0.045	−5.470 ± 0.010	197.105 ± 0.157	−7.976 ± 0.054
4.980	28.768 ± 0.011	−5.732 ± 0.011	−4.366 ± 0.002	194.713 ± 0.163	−7.905 ± 0.023
5.400	28.637 ± 0.023	−5.863 ± 0.023	−3.486 ± 0.004	183.005 ± 0.185	−7.745 ± 0.038
5.830	28.515 ± 0.043	−5.985 ± 0.043	−2.629 ± 0.007	160.908 ± 0.141	−7.518 ± 0.053
6.220	28.424 ± 0.011	−6.076 ± 0.011	−1.878 ± 0.002	130.993 ± 0.084	−7.245 ± 0.025
6.660	28.363 ± 0.044	−6.137 ± 0.044	−1.079 ± 0.007	86.127 ± 0.091	−6.856 ± 0.053
7.060	28.282 ± 0.033	−6.218 ± 0.033	−0.369 ± 0.005	33.103 ± 0.063	−6.479 ± 0.044
7.460	28.205 ± 0.024	−6.295 ± 0.024	0.324 ± 0.003	−32.534 ± 0.018	−6.053 ± 0.033
7.880	28.144 ± 0.027	−6.356 ± 0.027	1.009 ± 0.003	−112.635 ± 0.093	−5.562 ± 0.035
8.310	28.102 ± 0.011	−6.398 ± 0.011	1.703 ± 0.001	−211.496 ± 0.148	−4.983 ± 0.022

Table 7. Values of Molar Enthalpies of Dissolution of $C_8H_{17}NH_3 \cdot H_2PO_4$ (s) at Different Molalities at T = 298.15 K

$10^3\,m$	$\Delta_s H_m$	$^{\Phi}L$		$\bar{L}_1$	$\bar{L}_2$
$mol \cdot kg^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$10^5\,(\partial^{\Phi}L/\partial m)_{T,P}$	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
0.888	21.533 ± 0.032	−0.787 ± 0.032	−8.510 ± 0.036	12.080 ± 0.051	−1.543 ± 0.043
1.340	21.116 ± 0.028	−1.204 ± 0.028	−7.574 ± 0.021	24.556 ± 0.063	−2.221 ± 0.033
1.770	20.803 ± 0.013	−1.517 ± 0.013	−6.831 ± 0.007	38.355 ± 0.043	−2.723 ± 0.026
2.200	20.486 ± 0.042	−1.834 ± 0.042	−6.159 ± 0.019	53.634 ± 0.061	−3.188 ± 0.027
2.650	20.199 ± 0.023	−2.121 ± 0.023	−5.529 ± 0.009	69.939 ± 0.073	−3.586 ± 0.053
3.080	19.963 ± 0.041	−2.357 ± 0.041	−4.979 ± 0.013	85.084 ± 0.088	−3.891 ± 0.034
3.990	19.633 ± 0.046	−2.687 ± 0.046	−3.943 ± 0.012	112.812 ± 0.102	−4.259 ± 0.058
4.420	19.489 ± 0.024	−2.831 ± 0.024	−3.489 ± 0.005	122.885 ± 0.102	−4.375 ± 0.036
4.850	19.362 ± 0.043	−2.958 ± 0.043	−3.065 ± 0.009	130.007 ± 0.093	−4.445 ± 0.059
5.330	19.212 ± 0.014	−3.108 ± 0.014	−2.624 ± 0.003	133.982 ± 0.156	−4.506 ± 0.023
5.720	19.117 ± 0.022	−3.203 ± 0.022	−2.271 ± 0.004	133.811 ± 0.123	−4.503 ± 0.034
6.170	19.018 ± 0.014	−3.302 ± 0.014	−1.885 ± 0.002	129.244 ± 0.267	−4.465 ± 0.023
6.620	18.942 ± 0.017	−3.378 ± 0.017	−1.514 ± 0.003	119.544 ± 0.103	−4.380 ± 0.023
7.500	18.838 ± 0.026	−3.482 ± 0.026	−0.832 ± 0.005	84.261 ± 0.009	−4.106 ± 0.033
7.940	18.789 ± 0.036	−3.531 ± 0.036	−0.511 ± 0.002	57.913 ± 0.002	−3.936 ± 0.042
8.370	18.753 ± 0.017	−3.567 ± 0.017	−0.203 ± 0.002	25.615 ± 0.001	−3.737 ± 0.023
8.820	18.725 ± 0.011	−3.595 ± 0.011	0.108 ± 0.001	−15.146 ± 0.004	−3.499 ± 0.023

compounds are measured by means of the isoperibol solution-reaction calorimeter. The experimental values of enthalpies of dissolution of the compound in the water, the apparent relative molar enthalpies ($^{\Phi}L$), and the relative partial molar enthalpies ($\bar{L}_2$ and $\bar{L}_1$) of the compound and the solvent at different concentrations are listed in Tables 6 and 7. The curves of molar enthalpies of dissolution as a function of the molality m are plotted in Figures 5 and 6.

Molar Enthalpies of Dissolution at Infinite Dilution and Pitzer's Parameters. From eqs 2 and 3, the working equation to determine Pitzer's parameters is:[10]

$$Y = \frac{\Delta_s H_m - 2\left(\frac{A_H}{2.4}\right)\ln(1 + 1.2I^{1/2})}{2RT^2} = a_0 - m\beta_{MX}^{(0)L} - my'\beta_{MX}^{(1)L} - \frac{m^2 C_{MX}^{\Phi L}}{2} \qquad (6)$$

where Y is the extrapolation function, $a_0 = (\Delta_s H_m^{\infty})/(2RT^2)$, and $y' = [1 - (1 + 2I^{1/2})\exp(-2I^{1/2})]/2I$.

As for n-nonylammonium dihydrogen phosphate, regression of Y against $-m$ and $-my'$ is made by least-squares to obtain $\alpha_0 = 2.334 \cdot 10^{-2}$, $\beta_{MX}^{(0)L} = -9.923$, and $\beta_{MX}^{(1)L} = 11.781$ with a standard deviation of fit of $8.66321 \cdot 10^{-5}$ and correlation coefficient of 0.99396. The molar enthalpy of dissolution of n-nonylammonium dihydrogen phosphate at infinite dilution is calculated to be $\Delta_s H_m^{\infty} = 34.50\ kJ \cdot mol^{-1}$. The 3D graphics of regression of Y against $-m$ and $-my'$ is plotted in Figure 7.

As for n-octylammonium dihydrogen phosphate, regression of Y against $-m$ and $-my'$ is made by least-squares to obtain $\alpha_0 = 1.51 \cdot 10^{-2}$, $\beta_{MX}^{(0)L} = -4.376$, and $\beta_{MX}^{(1)L} = 5.279$ with a standard deviation of fit of $2.72091 \cdot 10^{-5}$ and correlation coefficient of 0.99825. The molar enthalpy of dissolution of n-octylammonium dihydrogen phosphate at infinite dilution is calculated to be $\Delta_s H_m^{\infty} = 22.32\ kJ \cdot mol^{-1}$. The 3D graphics of regression of Y against $-m$ and $-my'$ is plotted in Figure 8.

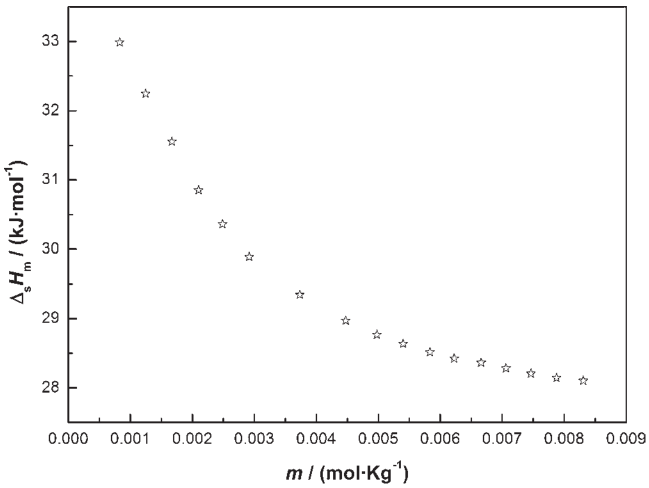

Figure 5. Plot of the measured $\Delta_s H_m$ against molality for $C_9H_{19}NH_3 \cdot H_2PO_4$(s).

The values of molar enthalpies of dissolution of the two compounds at infinite dilution indicate that the dissolutions of n-nonylammonium dihydrogen phosphate and n-octylammonium dihydrogen phosphate are all endothermic processes; this may be ascribed to the existence of a hydrophobic alkyl group in the title compounds, which leads to the weakening of hydration effect of the compound when meeting with the solvent. Moreover, the breaking of hydrogen bonds existing in the substance needs to absorb additional heat. Therefore, the endothermic process takes place because the heat quantity given off from hydration of the compound is smaller than that absorbed due to the breaking of ionic bonds and hydrogen bonds in the solid compound. n-Nonylammonium dihydrogen phosphate has one additional methylene in comparison with n-octylammonium dihydrogen phosphate. The methylene is a hydrophobic group. When dissolved in the water, n-nonylammonium ethylenediamine

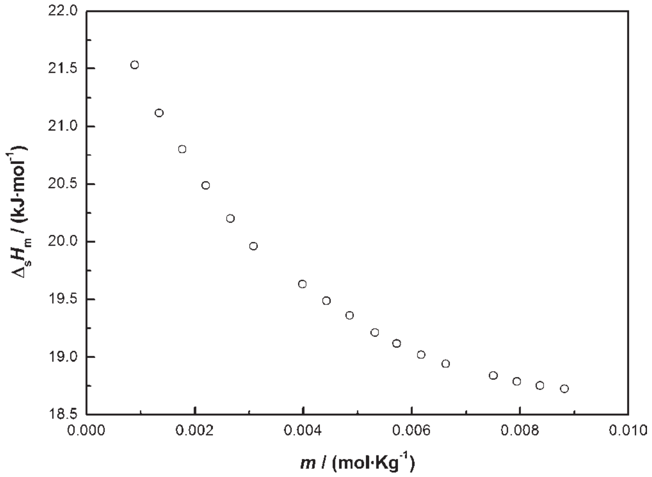

Figure 6. Plot of the measured $\Delta_s H_m$ against molality for $C_8H_{17}NH_3 \cdot H_2PO_4(s)$.

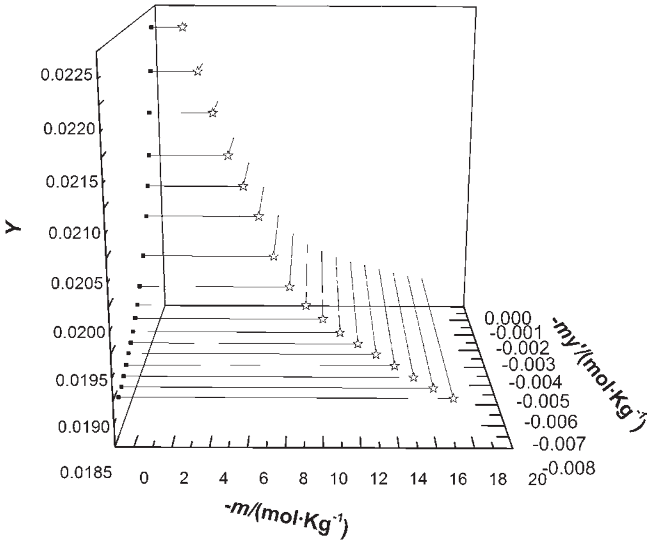

Figure 7. 3D graphics of regression of Y against $-m$ and $-my'$ for *n*-nonylammonium dihydrogen phosphate.

dihydrochloride needs more energy to make the hydrophobic group enter the aqueous solution. So $\Delta_s H_m^\infty$ ($C_9H_{19}NH_3 \cdot H_2PO_4$) is higher than $\Delta_s H_m^\infty$ ($C_8H_{17}NH_3 \cdot H_2PO_4$).

$\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$ are attributed to the short-range interaction between the cation and the anion. The absolute values of $\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$ are very small for the usual electrolyte and have the tendency to increase along with the volume and the quantity of the ion. The absolute values of $\beta_{MX}^{(0)L}$ and $\beta_{MX}^{(1)L}$ of the two compounds, and the experimental results conform to this tendency. $\beta_{MX}^{(0)L}(C_9H_{19}NH_3 \cdot H_2PO_4)$ and $\beta_{MX}^{(0)L}(C_8H_{17}NH_3 \cdot H_2PO_4)$ are both negative values, that is, $((\partial \beta_{MX}^{(0)})/(\partial T))_p < 0$, which indicates that the value of ${\beta_{MX}}^{(0)L}$ drops with the rise of the temperature. This shows that the interionic repulsive force decreases with the increase of the temperature.

Relative Partial Molar Enthalpies of the Title Compounds. The relative partial molar enthalpy is an important thermodynamic property of the electrolyte solution. Generally, there are many ways to determine the relative partial molar enthalpy. It can be conveniently obtained by the apparent relative molar enthalpy ($^{\Phi}L$) and partial derivative of $^{\Phi}L$ against m, $\partial^{\Phi}L/\partial m$:[10]

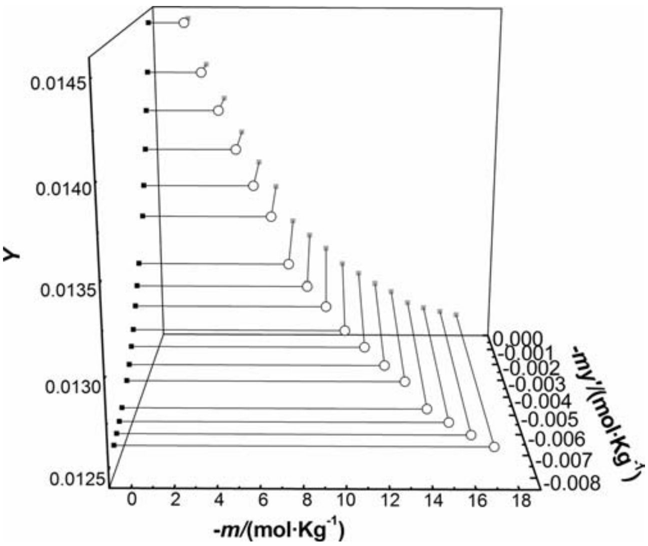

Figure 8. 3D graphics of regression of Y against $-m$ and $-my'$ for *n*-octylammonium dihydrogen phosphate.

$$\overline{L}_2 = {}^{\Phi}L + m(\partial^{\Phi}L/\partial m)_{T,P} \tag{7}$$

Partial derivative of $^{\Phi}L$ against m, $(\partial^{\Phi}L/\partial m)$, is obtained from the eq 5 under constant pressure and temperature:

$$\left(\frac{\partial^{\Phi}L}{\partial m}\right)_{T,P} = \frac{A_H}{2(m^{1/2} + 1.2m)} - 2RT^2[\beta_{MX}^{(0)L} + \beta_{MX}^{(1)L}\exp(-2m^{1/2}) + mC_{MX}^{\Phi L}] \tag{8}$$

The relative partial molar enthalpy ($\overline{L}_1$) of the redistilled water as the solvent is expressed as:

$$\overline{L_1} = -M_{H_2O}m^2\left(\frac{\partial^{\Phi}L}{\partial m}\right)_{T,P} \tag{9}$$

According to the relationship shown in eqs 7, 8, and 9, apparent relative molar enthalpy ($^{\Phi}L$) and relative partial molar enthalpy ($\overline{L}_2$ and $\overline{L}_1$) of the compound and the double-distilled water as the solvent are obtained. All of the results calculated above are listed in Tables 6 and 7. From Tables 6 and 7, we can see that the value of the relative partial molar enthalpy ($\overline{L}_1$) of the redistilled water increases at first and then decreases with increasing concentration. On the contrary, $\overline{L}_2$ decreases first and then increases with increasing concentration.

■ CONCLUSIONS

n-Nonylammonium dihydrogen phosphate and *n*-octylammonium dihydrogen phosphate are synthesized. The crystal structures of the two title compounds are determined by X-ray crystallography. The lattice potential energies and other thermodynamic properties of the two compounds are reported. The molar enthalpy of dissolution of the two title compounds at infinite dilution are determined to be 34.50 kJ·mol^{-1} and 22.32 kJ·mol^{-1} through Pitzer's theory, respectively. These results indicate that the endothermic reactions take place when the two compounds are dissolved in the double-distilled water.

AUTHOR INFORMATION

Corresponding Author

*Fax: +86−0635−8239121. E-mail: diyouying@126.com, diyouying@lcu.edu.cn.

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REFERENCES

(1) Cemil, A.; Sari, A.; Karaipekli, A. Preparation, thermal properties and thermal reliability of microencapsulated n−eicosane as novel phase change material for thermal energy storage. *Energy Convers. Manage.* **2011**, *52*, 687–692.

(2) Li, H.; Liu, X.; Fang, G. Y. Preparation and characteristics of n-nonadecane/cement composites as thermal energy storage materials in buildings. *Energy Build.* **2010**, *42* (10), 1661–1665.

(3) Arend, H.; Huber, W.; Mischgofsky, F. H.; Richter-Van Leeuwen, G. K. J. Layer perovskites of the $(C_nH_{2n+1}NH_3)_2MX_4$ and $NH_3(CH_2)_mNH_3MX_4$ families with M = Cd, Cu, Fe, Mn or Pd and X = Cl or Br: Importance, solubilities and simple growth techniques. *Cryst. Growth* **1978**, *43*, 213–223.

(4) Yin, H. D.; Chen, S. W.; Li, L. W.; Wang, D. Q. Synthesis, characterization and crystal structures of the organotin (IV) compounds with the Schiff base ligands of pyruvic acid thiophene-2-carboxylic hydrazone and salicylaldehyde thiophene-2-carboxylic hydrazone. *Inorg. Chim. Acta* **2007**, *360*, 2215–2223.

(5) Di, Y. Y.; Tan, Z. C.; Li, L. W.; Gao, S. L.; Sun, L. X. Thermochemistry on the coordination compounds of zinc sulphate with several L-α-amino acids. *J. Chem. Thermodyn.* **2006**, *38* (7), 884–888.

(6) Rychly, R.; Pekarek, V. The Use of Potassium Chloride and Tris-(hydroxymethyl) Aminomethane as Standard Substances for Solution Calorimetry. *J. Chem. Thermodyn.* **1977**, *9*, 391–396.

(7) Fábry, J.; Petrícek, A. V.; Kroupaaa, J.; Císarovａb, I. Ferroelastic structures of *n*-pentyl-, *n*-hexyl- and *n*-nonylammonium dihydrogenphosphate crystals. *Int. Union Crystallogr.* **2000**, *56* (5), 906–914.

(8) Oliver, S. R.; Lough, A. J.; Ozin, G. A. Crystal Structures of a Series of Novel Alkylammonium Phosphates and Their Formation in Aluminophosphate Synthesis Mixtures. *Inorg. Chem.* **1998**, *37*, 5021–5028.

(9) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J. L. Relationships among Ionic Lattice Energies, Molecular (Formula Unit) Volumes, and Thermochemical Radii. *Inorg. Chem.* **1999**, *38* (16), 3609–3622.

(10) Pitzer, K. S. *Activity Coefficients in Electrolyte Solutions*, revised ed.; CRC Press: Boca Raton, FL, 1991; Chapter 3.