(3) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969).
(4) L. F. Hohnstedt and D. T. Haworth, *J. Am. Chem. Soc.*, **82**, 89 (1960).
(5) O. T. Beachley, Jr., *Inorg. Chem.*, **8**, 981 (1969).
(6) M. P. Nadler and R. F. Porter, *Inorg. Chem.*, **8**, 599 (1969).
(7) H. Bock and W. Fuss, *Angew. Chem., Int. Ed. Engl.*, **10**, 182 (1971).
(8) V. G. Anicich and M. T. Bowers, *J. Am. Chem. Soc.*, **96**, 1279 (1974).
(9) N. C. Baird and M. A. Whitehead, *Can. J. Chem.*, **45**, 2059 (1967).
(10) A. W. Laubengayer and O. T. Beachley, *Adv. Chem. Ser.*, **No. 42**, 281 (1964).
(11) J. J. Solomon and R. F. Porter, *J. Am. Chem. Soc.*, **94**, 1443 (1972).
(12) J. Kroner, D. Proch, W. Fuss, and H. Bock, *Tetrahedron*, **28**, 1585 (1972).
(13) L. J. Turbini, T. J. Mazanec, and R. F. Porter, *J. Inorg. Nucl. Chem.*, **37**, 1129 (1975).
(14) K. Ryan, *J. Chem. Phys.*, **53**, 3844 (1970).
(15) R. A. Fluegge and D. A. Landman, *J. Chem. Phys.*, **54**, 1576 (1971).
(16) D. K. Bohme and F. C. Fehsenfeld, *Can. J. Chem.*, **47**, 2715 (1969).
(17) L. W. Sieck, L. Heller, and R. Gorden, Jr., *Chem. Phys. Lett.*, **10**, 502 (1971).
(18) An upper limit of 1 × 10^{-13} cm^3 molecule^{-1} sec^{-1} has been placed on the reaction $NH_3^+ + H_2 \rightarrow NH_4^+ + H$ by E. Herbst and W. Klemperer, *Astrophys. J.*, **185**, 505 (1973). This reaction is much too slow to account for the increased NH_4^+ intensity.
(19) D. C. Frost, F. G. Herring, C. A. McDowell, and I. A. Stenhouse, *Chem. Phys. Lett.*, **5**, 291 (1970).
(20) A. Serafini and J. F. LaBarre, *J. Mol. Structure*, **26**, 129 (1975).
(21) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **94**, 6901 (1972).
(22) W. Harshbarger, G. Lee, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, **8**, 1683 (1969).
(23) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **91**, 5350 (1969).
(24) L. D. Betowksi, J. J. Solomon, and R. F. Porter, *Inorg. Chem.*, **11**, 424 (1972).
(25) M. S. Munson and F. H. Field, *J. Am. Chem. Soc.*, **87**, 3294 (1965).
(26) E. D. Loughram, C. L. Malder, and W. E. McQuistion, Atomic Energy Commission Report LA-2368, 1960.
(27) V. I. Vedeneer, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities", Edward Arnold Ltd., London, 1966.
(28) L. J. Turbini, G. M. Golenwski, and R. F. Porter, *Inorg. Chem.*, **14**, 691 (1975).

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Basicity and Ion–Molecule Reactions of Trimethylarsine in the Gas Phase Determined by Ion Cyclotron Resonance Spectroscopy

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The gas-phase ion–molecule reactions of trimethylarsine have been investigated by ion cyclotron resonance spectroscopy. Reaction pathways, rate constants, and product distributions were determined by the variation of electron energy and by trapped-ion and double-resonance techniques. The parent ion reacts with $(CH_3)_3As$ to give $(CH_3)_5As_2^+$ and a methyl radical. The two principal fragment ions, $(CH_3)_2As^+$ and $C_2H_4As^+$, react to give the protonated parent ion and also undergo condensation reactions. The gas-phase basicity (proton affinity) of trimethylarsine is determined to be 209.3 kcal/mol [relative to PA(NH_3) = 201 kcal/mol] from investigations of proton-transfer equilibria. This result is consistent with previously established trends in the basicities of group 5 hydrides and their methyl derivatives.

Introduction

The gas-phase ion chemistry of the series $(CH_3)_nEH_{3-n}$, where E is a group 5 element, has been the subject of several studies. Molecules which have been examined include NH_3,[3–9] CH_3NH_2,[5,10–12] $(CH_3)_2NH$,[5,10–12] $(CH_3)_3N$,[5,10–12] PH_3,[8,13–18] CH_3PH_2,[19] $(CH_3)_2PH$,[19] $(CH_3)_3P$,[19] and AsH_3.[18,20] Of particular interest are the trends in gas-phase basicity of these compounds. Comparison of gas-phase basicities with condensed phase values, when the latter data are available, yields quantitative information on the effect of solvation on basicity.[11,19,21–23]

This paper reports the investigation by ion cyclotron resonance (ICR) spectroscopy of the gas-phase ion chemistry and basicity of $(CH_3)_3As$ for the purpose of comparison with previously studied congeneric compounds.

Experimental Section

The general features of ICR instrumentation and its operation in trapped-ion experiments have been previously described.[24–26] All experiments were performed at room temperature.

Reaction paths were identified by observing reactant and product ion intensities as a function of electron energy[16,27] and by double-resonance experiments.[24] Spectral intensities in the figures have been corrected to ion abundance by dividing the measured intensity by ion mass.[24,25]

Pressure measurements were made using a Schulz-Phelps gauge located adjacent to the ICR cell. This gauge is calibrated for each gas for a given emission current (5 μA) and magnetic field (6 kG) against an MKS Instruments Baratron Model 90H1-E capacitance manometer in the region 10^{-5}–10^{-3} Torr, where linear variation of gauge current with pressure is observed. Pressures in the trapped ion experiments were in the range 10^{-7}–10^{-5} Torr. The principal error in the rate constants (estimated to be ±20%) arises from uncertainties in pressure measurements. Mass spectra of $(CH_3)_3As$ recorded with the Schulz-Phelps gauge on and off demonstrated that no significant pyrolysis was occurring on the filament.

$(CH_3)_3As$ was obtained from Alfa Products. Mass spectral analysis revealed no detectable impurities. $CF_3(CH_2)_3NH_2$ was provided by Professor R. W. Taft (University of California, Irvine, Calif.). Other chemicals were readily available reagent grade materials and were used as supplied except for treatment using freeze–pump–thaw cycles to remove noncondensable impurities.

Results

Mass Spectrum. The mass spectrum of $(CH_3)_3As$ at low pressure (10^{-6} Torr) at 70 eV agreed with the reported spectrum.[28] The fragments present at 18 eV, the electron energy at which the trapped ion experiments were performed, include $(CH_3)_3As\cdot^+$ (*m/e* 120, 38%), $(CH_3)_2As^+$ (*m/e* 105, 35%), $C_2H_4As^+$ (*m/e* 103, 25%), and $C_2H_2As^+$ (*m/e* 101, 2%).

Ion–Molecule Reactions. Figures 1 and 2 illustrate the variation of ion abundance with time.[29] The principal reactions in $(CH_3)_3As$ parallel those of $(CH_3)_3P$.[19] Like $(CH_3)_3P\cdot^+$, the parent ion $(CH_3)_3As\cdot^+$ (*m/e* 120) does not react to give the protonated parent ion. Instead it undergoes exclusively the condensation reaction 1 to form $(CH_3)_5As_2^+$ (*m/e* 225), which is also formed in the clustering reaction 3 of $(CH_3)_2As^+$ (*m/e* 105) with the parent neutral.

$$(CH_3)_3As\cdot^+ + (CH_3)_3As \rightarrow (CH_3)_5As_2^+ + CH_3\cdot \tag{1}$$

$$(CH_3)_2As^+ + (CH_3)_3As \left\{ \begin{array}{ll} \xrightarrow{85\%} (CH_3)_3AsH^+ + C_2H_5As & (2) \\ \xrightarrow{10\%} (CH_3)_5As_2^+ & (3) \\ \xrightarrow{5\%} (CH_3)_4As_2\cdot^+ + CH_3\cdot & (4) \end{array} \right.$$

Other reactions of $(CH_3)_2As^+$ include proton transfer to

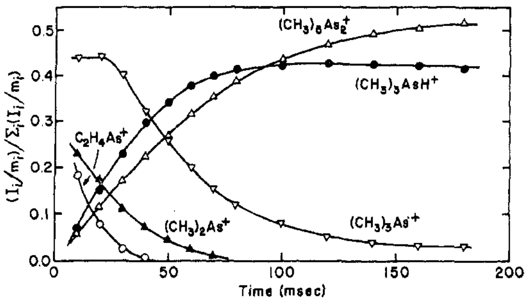

Figure 1. Temporal variation of ion concentrations for the major ions in trimethylarsine at 1.7 × 10^{-6} Torr pressure and 18 eV electron energy.

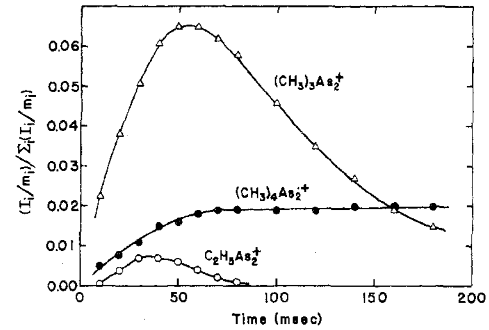

Figure 2. Temporal variation of ion concentrations for the minor ions in trimethylarsine (conditions same as Figure 1).

Table I. Rate Constants for the Disappearance of the Primary Ions in Trimethylarsine[a]

Primary ion	k^b
$(CH_3)_3As^{\cdot +}$	4.2
$(CH_3)_2As^+$	9.0
$C_2H_4As^+$	13.0

[a] All data from trapped-ion studies at 18 eV. [b] In units of 10^{-10} cm³ molecule⁻¹ sec⁻¹. Each constant is an average of three determinations. Accuracy in rate constants estimated to be ±20% due to uncertainties in pressure measurement.

the parent neutral, reaction 2, and the condensation reaction 4 to produce $(CH_3)_4As_2^{\cdot +}$ (*m/e* 210) with loss of a methyl radical. This reaction is noteworthy in that radicals are produced by two even-electron species. Such a process is usually energetically unfavorable. It is interesting to consider the possibility that the product ion in reaction 4 is tetramethyldiarsine, since the radical ion of this species is significantly stabilized by lone-pair interactions.[30]

In a process which formally involves transfer of As^+, $C_2H_4As^+$ (*m/e* 103) reacts to give $(CH_3)_3As_2^+$ (*m/e* 195), reaction 5. This As^+ transfer reaction is analogous to the P^+ transfer reactions observed in the phosphines.[19] The protonated parent is also formed by proton transfer from $C_2H_4As^+$, reaction 6. In the minor condensation reaction 7, $C_2H_4As^+$ reacts to form $C_2H_5As_2^+$ (*m/e* 179).

$$C_2H_4As^+ + (CH_3)_3As \begin{cases} \xrightarrow{60\%} (CH_3)_3As_2^+ + C_2H_4 & (5) \\ \xrightarrow{30\%} (CH_3)_3AsH^+ + C_2H_3As & (6) \\ \xrightarrow{10\%} C_2H_5As_2^+ + C_3H_8 & (7) \end{cases}$$

A high-mass ion, *m/e* 315, corresponding to $(CH_3)_6As_3^+$, is produced by the clustering reaction 8 of $(CH_3)_3As_2^+$ (*m/e* 195) with the parent neutral. Due to their low intensity and poor resolution at high mass, other possible high-mass products were not identified. The secondary ion $C_2H_5As_2^+$ (*m/e* 179) decreases in intensity at long times, possibly forming such a high-mass condensation product.

$$(CH_3)_3As_2^+ + (CH_3)_3As \rightarrow (CH_3)_6As_3^+ \qquad (8)$$

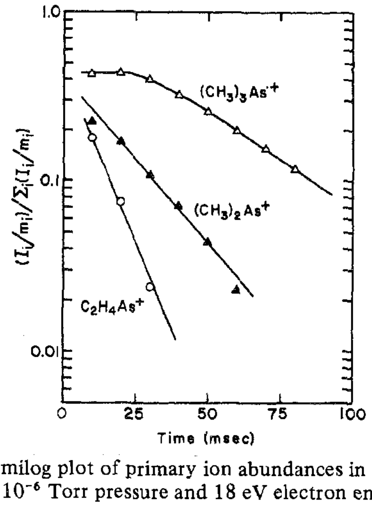

Figure 3. Semilog plot of primary ion abundances in trimethylarsine at 1.7 × 10^{-6} Torr pressure and 18 eV electron energy (data from Figure 1).

From the limiting slopes for the disappearance of the initially formed ions (Figure 3), total rate constants are calculated. The results are summarized in Table I.

Basicity of $(CH_3)_3As$. The gas-phase basicity (proton affinity) of a base B is defined as the standard enthalpy change for reaction 9. For two bases B_1 and B_2, a knowledge of the preferred direction of the proton-transfer reaction 10 establishes the sign of the free energy change for the reaction, ΔG.[31] If the proton affinities differ by no more than 3 kcal, equilibrium between B_1H^+ and B_2H^+ can often be observed in an ICR trapped-ion experiment. The free energy change for reaction 10 is calculated from the measured equilibrium constant according to $\Delta G = -RT \ln K$. If it is assumed that entropy effects are small and are limited to changes in rotational symmetry numbers, then the relative basicities, $\Delta H = PA(B_1) - PA(B_2)$, are readily calculated.[32,33] An absolute measurement of either $PA(B_1)$ or $PA(B_2)$ then automatically gives the other.

$$BH^+ \rightarrow B + H^+ \qquad \Delta H = PA(B) \qquad (9)$$

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1 \qquad (10)$$

The basicity of $(CH_3)_3As$ (Tables II and III) was determined from the equilibrium constants found for reaction 10, where $B_1 = (CH_3)_3As$ and $B_2 = CH_3NH_2$ or $CF_3(CH_2)_3NH_2$. These data, summarized in Table II, yield $PA[(CH_3)_3As] = 209.3 \pm 0.1$ kcal/mol.

Homolytic Bond Dissociation Energy of $(CH_3)_3AsH^+$. The homolytic bond dissociation energy of BH^+ is given by the standard enthalpy change for reaction 11. This quantity is related to the basicity of B by the adiabatic ionization po-

$$BH^+ \rightarrow B^+ + H \qquad \Delta H = D(B^+\text{-}H) \qquad (11)$$

Table II. Basicity of Trimethylarsine Derived from Equilibrium Constants for Proton-Transfer Reactions

$(CH_3)_3AsH^+ + B \rightleftharpoons BH^+ + (CH_3)_3As$	K^a	ΔG^b	ΔH^b	$PA(B)^{c,d}$	$PA[(CH_3)_3As]^d$
$(CH_3)_3AsH^+ + CH_3NH_2 \rightleftharpoons CH_3NH_3^+ + (CH_3)_3As$	0.9	0.05	−0.6	209.9	209.3
$(CH_3)_3AsH^+ + CF_3(CH_2)_3NH_2 \rightleftharpoons CF_3(CH_2)_3NH_3^+ + (CH_3)_3As$	4.8	−0.9	−1.6	210.9	209.3

[a] Average of at least three independent determinations. [b] In kcal/mol. [c] Reference 23. [d] Basicity (proton affinity) in kcal/mol. All data relative to $PA(NH_3)$ = 201 kcal/mol (see Table III).

Table III. Gas-Phase Basicities, Adiabatic Ionization Potentials, and $D(B^+-H)$ Homolytic Bond Dissociation Energies for the Group 5 Hydrides and Their Methyl Derivatives

Molecule	PA[a,b]	IP[a,c]	$D(B^+-H)$[a]
NH_3	201[d]	235.0	122.4
$MeNH_2$	209.9	206.8	103.1
Me_2NH	216.1	190.0	92.5
Me_3N	220.2	180.3	86.9
PH_3	187.2[e]	229.6	103.2
$MePH_2$	200.9	210.2	97.5
Me_2PH	212.5	195.3	94.2
Me_3P	221.4	184.7	92.5
AsH_3	180.7[e]	228[f]	95
Me_3As	209.3	182[g]	78

[a] In kcal/mol. [b] Data are from ref 23, except as noted. All proton affinities were determined relative to PA(NH_3). [c] Data are from ref 19, except as noted. [d] Recent experiments in our laboratory and at the University of California (Irvine, Calif.) have demonstrated that PA(NH_3) is lower than the generally accepted value of 207 kcal/mol (see ref 7). Equilibrium proton-transfer reactions give a value of PA(NH_3) = 201 ± 1 kcal/mol relative to eight reference species (alkenes and carbonyl compounds). This result is also confirmed by recent studies of Kebarle and coworkers (presented at the 23rd Annual ASMS Meeting, Houston, Tex., 1975). [e] J. F. Wolf, I. Koppel, R. W. Taft, R. H. Staley, and J. L. Beauchamp, to be submitted for publication. [f] A. W. Potts and W. C. Price, *Proc. R. Soc. London, Ser. A*, **326**, 181 (1972). [g] Reference 34.

tentials of B and H· in eq 12. The adiabatic ionization

$$D(B^+-H) = PA(B) + IP(B) - IP(H) \qquad (12)$$

potential of $(CH_3)_3As$ has been determined by photoelectron spectroscopy to be 7.9 eV (182 kcal/mol).[34] This yields the homolytic bond dissociation energy $D[(CH_3)_3As^+-H]$ = 78 kcal/mol.

Discussion

The ion chemistry of arsine[20] and trimethylarsine is similar to that of phosphine[16] and the methylphosphines,[19] with both series differing from the related amines.[5,10] Proton transfer to the parent neutral dominates the ion chemistry of the amines. In addition to proton-transfer reactions the phosphines and arsines also undergo condensation reactions with the elimination of a small molecule or radical fragments and probably the formation of P–P and As–As bonds. Condensation reactions give over 50% of the product ions in $(CH_3)_3P$ and $(CH_3)_3As$, whose parent ions do not react to form protonated parent ions. One of the notable features of Figures 1 and 3 is that the parent ion, $(CH_3)_3As\cdot^+$, is initially unreactive. It may be formed in a relatively unreactive excited state which then is collisionally deactivated. A pronounced reduction in reaction rate with increasing internal energy has been observed for $(CH_3)_3N$.[10]

The gas-phase basicities of the group 5 hydrides and their methyl derivatives are given in Table III. Successive methyl substitution increases basicity. Compared to the effects in the phosphines and arsines, this effect is much less pronounced in the amines. It has been argued[19] that methyl substitution increases the rehybridization energy required to go from an unprotonated to a protonated amine. This works against the inductive effect of the methyl groups. The rehybridization energy in the phosphine series is essentially constant[35] and the inductive effect of the methyl groups predominates. A similar explanation may be offered for the arsines.

The decrease in BH^+ homolytic bond dissociation energies (Table III) with increasing methyl substitution in the amines has been attributed to stabilization of the radical cation vs. the protonated parent due to delocalization of charge and spin to the methyl substituents in the radical cation.[12,19] In the phosphines and the two arsines the dissociation energies are relatively constant. Delocalization is apparently less important in the radical cation of these compounds, because of poor orbital overlap.[19] This effect is also evident in comparing relative BH^+ homolytic bond dissociation energies of the trimethyl derivatives, with the observed order being P > N > As.

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References and Notes

(1) National Science Foundation Predoctoral Fellow.
(2) Dreyfus Teacher-Scholar.
(3) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *J. Chem. Phys.*, **39**, 1599 (1963).
(4) C. E. Melton, *J. Chem. Phys.*, **45**, 4414 (1966).
(5) M. S. B. Munson, *J. Phys. Chem.*, **70**, 2034 (1966).
(6) S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967).
(7) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969).
(8) D. Holtz and J. L. Beauchamp, *J. Am. Chem. Soc.*, **91**, 5913 (1969).
(9) W. T. Huntress, Jr., M. M. Mosesman, and D. D. Elleman, *J. Chem. Phys.*, **54**, 843 (1971).
(10) L. Hellner and L. W. Sieck, *Int. J. Chem. Kinet.*, **5**, 177 (1973).
(11) E. M. Arnett, F. M. Jones III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724 (1972).
(12) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4728 (1972).
(13) A. Giardini-Guidoni and G. G. Volpi, *Nuovo Cimento*, **17**, 919 (1960).
(14) M. Halmann and I. Platzner, *J. Phys. Chem.*, **71**, 4522 (1967).
(15) I. Platzner, *Isr. J. Chem.*, **6**, 34p (1968).
(16) D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Am. Chem. Soc.*, **92**, 7045 (1970).
(17) J. R. Eyler, *Inorg. Chem.*, **9**, 981 (1970).
(18) J. I. Brauman, J. R. Eyler, L. K. Blair, M. J. White, M. B. Comisarow, and K. C. Smyth, *J. Am. Chem. Soc.*, **93**, 6360 (1971).
(19) R. H. Staley and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 6252 (1974).
(20) R. H. Wyatt, D. Holtz, T. B. McMahon, and J. L. Beauchamp, *Inorg. Chem.*, **13**, 1511 (1974).
(21) M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 1369 (1972).
(22) R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *J. Am. Chem. Soc.*, **95**, 3811 (1973).
(23) R. W. Taft, *Prog. Phys. Org. Chem.*, **12**, 143 (1975).
(24) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(25) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).
(26) M. S. Foster and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 4808 (1975).
(27) J. L. Franklin, *J. Chem. Educ.*, **40**, 284 (1963).
(28) R. G. Kostyanovskii and V. V. Yakshin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **10**, 2363 (1967).
(29) The variation of the abundance of $(CH_3)_6As_3^+$ (*m/e* 315) with time was not recorded. Its intensity is not included in $\sum(I_i/m_i)$ in Figures 1–3.
(30) A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and M. C. Padulina, *J. Am. Chem. Soc.*, **96**, 2648 (1974).
(31) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93**, 4314 (1971).
(32) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968, p 37.
(33) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 3504 (1973).
(34) Estimated from the photoelectron spectrum published in S. Elbel, H. Bergmann, and W. EnBlin, *J. Chem. Soc., Faraday Trans. 2*, **70**, 555 (1974).
(35) M. F. Guest, I. H. Hillier, and V. R. Sanders, *J. Chem. Soc., Faraday Trans. 2*, **68**, 867 (1972); I. H. Hillier and V. R. Sanders, *J. Chem. Soc. D*, 316 (1970).