

critical regions (such as the ones labeled A, B, C, and D in these figures), more accurate information can be obtained about nonrandom reorganization equilibria by mixing compounds based on different central atoms (e.g., MX_n with QZ_p) than by mixing two different compounds based on the same central atom (e.g., MX_n with MZ_n).

The rapid and highly nonrandom equilibration exhibited by the systems investigated here is probably attributable to considerable rehybridization of the electronic orbitals of the phosphorus when a chlorine atom is substituted by an amino group or *vice versa*. The problem does not seem to be one of steric hindrance, since bis-(dialkylamino)-chlorophosphine and dialkylaminodichlorophosphine would not be expected to be equally efficacious in relieving any strain as-

sumed to exist in phosphorus trichloride and/or tris-(diethylamino)-phosphine. It is interesting to note that, in the system studied here and the related nonrandom systems¹³ $PCl_3-P(OC_2H_5)_3$ and $P(OC_2H_5)_3-P[N(C_2H_5)_2]_3$, the change in P^{31} n.m.r. chemical shifts when going from one to another in a series of compounds obtained by substituent interchange is nonlinear. In a number of cases where random sorting of substituents is observed at equilibrium, the chemical shifts generally vary linearly from compound to neighboring compound.

Acknowledgment.—We are indebted to Allan W. Dickinson for computing the curves shown in the figures.

(13) E. Fluck and J. R. Van Wazer, *Z. anorg. allgem. Chem.*, **307**, 113 (1961).

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, CENTRAL RESEARCH DEPARTMENT, ST. LOUIS, MISSOURI]

Exchange of Parts between Molecules at Equilibrium. IV. The New Family of Poly(fluoroarsenous methylimides)

BY MARVIN D. RAUSCH, JOHN R. VAN WAZER, AND KURT MOEDRITZER

RECEIVED OCTOBER 8, 1963

Dissolution of the cage compound, $As_4(NCH_3)_6$, in arsenic trifluoride gives homogeneous liquids which, by H^1 and F^{19} n.m.r., are seen to be made up of several structural entities. Interpretation of the proton n.m.r. data in terms of methylimino bridges between various combinations of end, middle, and branch structure-building units leads to the conclusion that interchange between halogens and bridging methylimino groups on the arsenic atoms is quite nonrandom, with the mixed species (the end and middle units) having relatively large negative heats of formation from the *neso* and branch units. The data also show that ring structures are not present in appreciable amounts throughout the composition region ranging from AsF_3 to an average over-all stoichiometry around $As_6F_8(NCH_3)_6$ in the $AsF_3-As_2(NCH_3)_3$ system. Within this composition range, the molecules are predominantly straight chains.

Polyatomic molecules based on backbones other than chains of carbon atoms often undergo exchange of parts between different molecules or within the same molecule at the temperatures involved in standard laboratory operations.¹ This means that the usual synthetic procedures give equilibrium distributions of the variously sized and shaped molecules which can be formed. In order to synthesize new families of compounds in which the higher molecular weight molecules are amenable to study (*i.e.*, they are not insoluble, amorphous, network polymers), one must find systems in which the end (monofunctional) and middle (difunctional) molecule building units occur at equilibrium in quantities greater than that expected from random sorting of the molecular parts exhibiting various functionalities. When middles and ends predominate, there will be composition regions in which the molecules are large but not sufficiently tied together by cross linking through branch units to form an infinite network (*i.e.*, the system will not be beyond the "gel point").

In previous studies² on *neso*³ compounds, we found that scrambling of amino groups with halogens on arsenic gave essentially quantitative yields of the mixed molecules at their respective stoichiometric compositions. It was therefore reasoned that exchange of a bridging nitrogen atom with halogens should lead to systems involving long straight chain molecules at the over-all composition corresponding to a halogen-arsenic mole ratio slightly greater than unity. This paper describes the use of n.m.r. in elucidating the

structures of the molecules present in the previously unknown system $AsF_3-As_2(NCH_3)_3$.

Experimental

Materials.—Arsenic trifluoride was obtained from the Chemicals Procurement Laboratories, Inc. Tetraarsenic hexamethylimide, $As_4(NCH_3)_6$, was prepared from arsenic trichloride and methylamine according to the directions⁴ of its discoverers. Dry reagent grade toluene was employed when a solvent was used.

Equilibration.—Depending on the equilibrium composition desired, from 0.2 g. to 2.0 g. of tetraarsenic hexamethylimide and from 3.3 g. to 0.2 g. of arsenic trifluoride were accurately weighed into 5 mm. i.d. thick-walled Pyrex tubes which had previously been kept in an oven to remove sorbed water and then flushed with pure, dry nitrogen. The tubes were sealed and then heated for 8 hr. at 130°. The contents of each tube were completely homogeneous under these conditions. After heating, the tubes were rapidly cooled to 0°. They were opened and were carefully warmed until the contents were again homogeneous. A portion of the contents was transferred directly into a precision-bore, thin-walled n.m.r. tube. The remaining material was dissolved in three parts of toluene and the resulting solution transferred into another n.m.r. tube. It was subsequently found that equilibrium was attained immediately upon dissolution of the $As_4(NCH_3)_6$.

Analytical Procedures.—Proton n.m.r. spectra were obtained on a Varian Model A-60 spectrometer, at 36° and a frequency of 60,000 Mc., generally using a sweep rate of 0.5 c.p.s. at the smallest available sweep width (50 cycles for full scan). As compared to the neat liquid, the toluene solution of a given equilibrium mixture generally provided much better resolution of the individual peaks. Moreover, the over-all spectra of the diluted and undiluted samples were similar, showing identical peak areas in those cases where the resolution with the neat liquid was adequate for area measurement ($R \equiv$ the F/As mole ratio > 1.5). As the proportion of $As_2(NCH_3)_3$ in the $AsF_3-As_2(NCH_3)_3$ mixtures was increased, the viscosity of the neat liquids rose precipitously so that, for an over-all composition less than that corresponding to the mole ratio $R \equiv F/As = 1.9$, some peaks could not be resolved, and below $R = 1.5$ all peaks had coalesced into a single broad hump. Upon combining $As_2(NCH_3)_3$ with AsF_3 , the number of proton resonances gradually increased from

(1) J. R. Van Wazer, *Am. Scientist*, **50**, 450 (1962).

(2) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139 (1964).

(3) The *neso* molecule is the smallest member of a family of compounds, being a central atom or moiety surrounded by monofunctional substituents. In the case of the system introduced herein, the *neso* compound is arsenic trifluoride.

(4) H. Noth and H. J. Vetter, *Naturwissenschaften*, **48**, 553 (1961).

one to more than a dozen, with extensive overlapping for equilibrium compositions having R values in the range of 0.5 to 0.8. For R values lower than *ca.* 0.5, the spectrum became less complicated, finally reducing to two peaks for solutions of the thermally equilibrated $\text{As}_2(\text{NCH}_3)_3$.

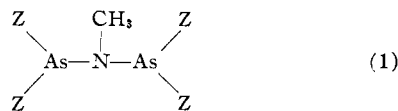
The chemical shifts of the various resolvable proton resonance peaks are presented at the top of Table II. These shifts were referenced to tetramethylsilane, as an internal standard. Quantitative determination of the individual n.m.r. peak areas for the various mixtures for which $R > 1.0$ and $R = 0.0$ was made by weighing cut-out Xerox copies of the peaks and also by electronic integration in the case of the simpler spectra. For $0 < R < 1.0$, extensive overlapping of the resonance peaks necessitated the use of peak heights for approximating their areas. Proper corrections, totaling no more than a few per cent of all hydrogens were made for: (1) side bands resulting from mechanical spinning of the sample, and (2) an interfering satellite peak due to the C^{13} splitting of the methyl protons of toluene, when solvent was used.

F^{19} n.m.r. spectra were obtained on a Varian Model HR-60 spectrometer operating at 27° and at a frequency of 56.444 Mc. All samples were spun in 5 mm. precision-bore thin-walled n.m.r. tubes. Peaks were referenced to trifluoroacetic acid as an external standard using the side-band technique. A single peak representing the total fluorine resonance was observed for both the neat liquids and the toluene solutions at compositions having $R \equiv \text{F}/\text{As} > 1.3$. As shown in Fig. 1, this peak shifted to a higher field and exhibited considerable broadening as the fluorine content of the equilibrium mixture was decreased. F^{19} n.m.r. measurements on toluene solutions at low temperatures caused this single peak to broaden without resolution into separate peaks. For toluene solutions of compositions having R values below unity, five reasonably sharp peaks appeared in addition to the broad peak. The shifts of these peaks are denoted in Fig. 1 by crosses. The most prominent of these five peaks for the compositions studied is the one at +13.5 p.p.m.

Viscosity measurements were carried out with a Gardner bubble viscometer.⁵

Results and Interpretation

Assignments in the Proton Spectra.—The observed presence of a number of different resonances in the H^1 n.m.r. spectra indicates that the chemical shift of protons in the methyl group of a methylimino bridge is sensitive to the arrangements of the atoms somewhat distantly placed in the molecule. In the simplest case, we can consider only the nearest groups about such a methylimino bridge in a molecule, which we call the second-order environment, *i.e.*



where Z is either a fluorine atom or a methylimino bridge, and the observed H^1 n.m.r. resonance is attributed to the hydrogens of the CH_3 group shown. When the two Z groups on one of the two arsenic atoms of eq. 1 are both fluorines, this arsenic is the central atom of an end group, *e*. Likewise, a middle group, *m*, corresponds to one of the two Z groups on this arsenic being a fluorine and the other an imino bridge, and a branch group, *b*, to both Z groups being imino bridges. The *neso* compound, $n = \text{AsF}_3$, does not appear in the proton spectra and must obviously be determined by difference from the stoichiometry.

There is a total of six H^1 n.m.r. resonances corresponding to the imino bridges (denoted hereafter by a — in the formulas) between (1) two ends, *e—e*; (2) an end and a middle, *e—m*; (3) two middles, *m—m*; (4) an end and a branch, *e—b*; (5) a middle and a branch, *m—b*; and (6) two branches, *b—b*. If the formation of ends and middles is greatly preferred over random sorting only five peaks should be seen, since ends and branches will not occur concomitantly to any appreciable amount. However, our spectra (see Table II) exhibit more than a dozen resonances and it seems

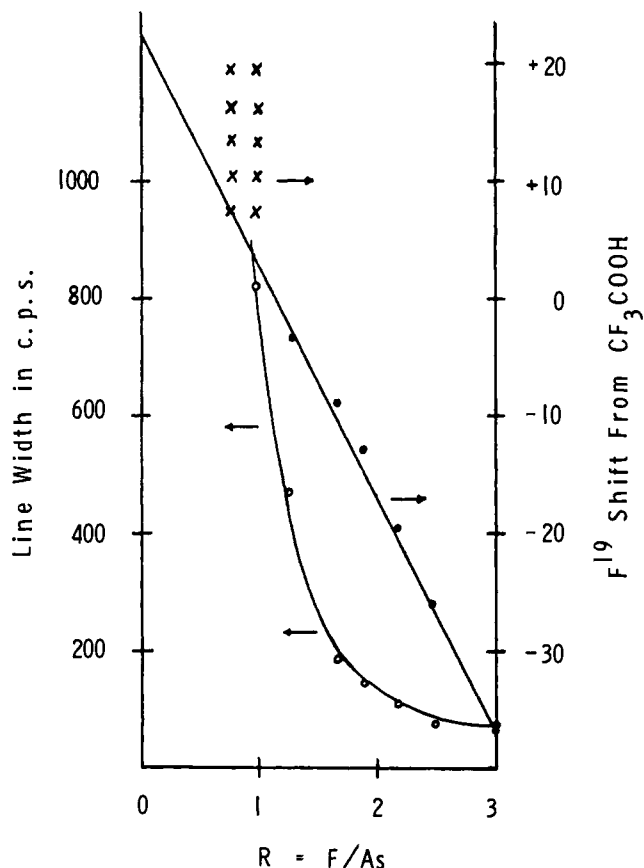
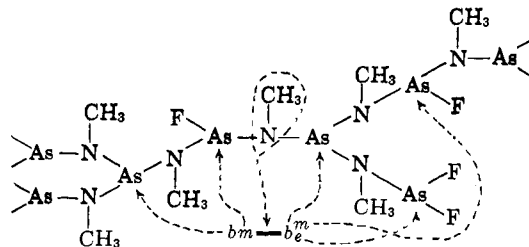


Fig. 1.— F^{19} n.m.r. chemical shifts and line widths at half-peak height for various values of $R = \text{F}/\text{As}$ in the system AsF_3 – $\text{As}_2(\text{NCH}_3)_3$. The solid and open circles correspond to the chemical shift and line width, respectively, of the observed broad resonance and the crosses to the chemical shifts of the relatively sharp peaks seen at low R values. The arrows show the proper scale to be used for each set of data.

most unlikely that the extra ones could be attributed to conformational effects or a host of different sized rings. Therefore, it is reasonable to consider a higher order of environment of building units around the bridging $\text{CH}_3\text{N}<$ which bears the hydrogens causing the given n.m.r. peak. Thus, for a fourth-order environment, the Z in formula 1 may be either a fluorine atom or an $-\text{N}(\text{CH}_3)-\text{AsY}_2$ grouping, where Y may again be either a fluorine atom or a methylimino bridge. Thus, for example, the following structure has one Z as a fluorine atom and the three other Z groupings as $-\text{N}(\text{CH}_3)-\text{AsY}_2$ having $Y = Y' = \text{CH}_3\text{N}<$ bridges for one, $Y = \text{CH}_3\text{N}<$ and $Y' = \text{F}$ for another, and $Y = Y' = \text{F}$ for the third. The *e—m—b* symbolic notation is given with the structural formula



Although there are 55 arrangements corresponding to a fourth-order environment of an $>\text{AsN}(\text{CH}_3)\text{As}<$ moiety, all of the respective n.m.r. peaks will not simultaneously appear for any fully or partially equilibrated mixture. Thus, when the R value of an equilibrated mixture is reduced slightly from 3 (corresponding to

(5) J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colwell, "Viscosity and Flow Measurement," Interscience Publishers, New York, N. Y., 1963, p. 283.

TABLE I
EQUATIONS FOR CALCULATING RELATIVE AREAS OF N.M.R.
PEAKS CORRESPONDING TO VARIOUS FOURTH-ORDER ARRANGEMENTS OF BUILDING UNITS ABOUT LINKAGES

| Specific linkage | Fraction of total peak areas as specific peak ^a |
|------------------|--|
| A | $e-e$ $[e]^2/A^2$ |
| | $e-me$ $2[e]^2(2[m])/A^3$ |
| | $e-mm$ $2[e](2[m])^2/A^3$ |
| B | $em-me$ $[e]^2(2[m])^2/A^4$ |
| | $em-mm$ $2[e](2[m])^3/A^4$ |
| | $mm-mm$ $(2[m])^4/A^4$ |
| C | $e-mb$ $2[e](2[m])(3[b])/A^3$ |
| | $em-mb$ $2[e](2[m])(3[b])/A^4$ |
| D | $e-b_m$ $2[e](2[m])^2(3[b])/A^4$ |
| | $e-b_e$ $2[e]^3(3[b])/A^4$ |
| E | $e-b_m^e$ $4[e]^2(2[m])(3[b])/A^4$ |
| | $mm-mb$ $2(2[m])^3(3[b])/A^4$ |
| | $bm-mb$ $(2[m])^2(3[b])^2/A^4$ |

^a $A = 3 - R = [e] + 2[m] + 3[b]$, with concentrations of building units being denoted by the appropriate symbol in brackets, [].

pure AsF_3), the first resonance to appear in the proton spectra will be that of the dimolecule (*i.e.*, a bridge between two end groups). For values of K_1 and K_2 , defined below in eq. 2 and 3, reasonably smaller than 0.33 (the value for random sorting^{1,6} of the fluorine atoms and methylimino bridges about the arsenic atoms), resonances corresponding to the linkages shown under A in Table I will predominate for compositions in the range of $3 > R > ca. 2.3$. Likewise, those denoted by B will be important for $2 > R > 1$, whereas those denoted by C will not be significant and those by D will not even appear when the constants of eq. 2 and 3 are much smaller than random. Resonances for the structures grouped under E will only be important for compositions near $R = 1$, and the structures containing large amounts of branches with middles must predominate for $R < 1$. The entire n.m.r. spectrum must correspond to structures based only on branched groups at $R = 0$.

Following this line of *a priori* reasoning, several of the n.m.r. peaks in the upper part of Table II are immediately identifiable. Thus, the resonance appearing at -2.78 p.p.m. is unquestionably attributable to the $e-e$ molecule because the relative area of this peak decreases monotonously with increasing R while its absolute area is found to increase rapidly as the value of R is first reduced from 3.0 in the range of $3 > R > 2$. Likewise, the resonance seen at -2.73 p.p.m. must be assigned to the $e-me$ arrangement, in accord with its early appearance and maximization at an R value somewhat greater than 2. Presumably the next peaks to appear at -2.91 p.p.m. and -2.80 p.p.m. also involve arrangement of end and middle groups unless one of them is attributable to $e-mb$. The peak at -2.91 p.p.m. is reasonably assigned to the $e-mm$ arrangement because of its early appearance and its maximization at $R = 1.6$. Probably the peak at -2.80 is due to a bridge between two m atoms involving an e in the second order of environment of the bridge (*i.e.*, $em-me$ or $em-mm$). The fact that, for high values of R , the area of this peak is approximately half of the areas of the peak at -2.91 p.p.m. favors an $em-me$ arrangement. However, the appearance of a maximum relative area of the -2.80 peak, at $R = 1.3$, corresponding to nearly one quarter of the total

(6) G. Calingaert and H. A. Beatty, *J. Am. Chem. Soc.*, **61**, 2748 (1939).

methylimino bridges, supports an $em-mm$ assignment for it.

Equilibrium between Building Units.—In accord with the rationale used in previous papers from this laboratory,⁷ we shall now attempt to evaluate the equilibrium constants

$$K_1 = [n][m]/[e]^2 \quad (2)$$

$$K_2 = [e][b]/[m]^2 \quad (3)$$

From stoichiometric considerations alone, it can be shown that the fraction of total units as ends, middles, and branches, respectively, are given by eq. 4–6, where \mathfrak{L} stands for the fraction of the total n.m.r. peak area corresponding to structures based on the bridge shown in parentheses immediately behind the subscript L

$$[e] = [(3 - R)/2][2\mathfrak{L}_{(e-e)} + \mathfrak{L}_{(e-m)} + \mathfrak{L}_{(e-b)}] \quad (4)$$

$$[m] = [(3 - R)/4][\mathfrak{L}_{(e-m)} + 2\mathfrak{L}_{(m-m)} + \mathfrak{L}_{(m-b)}] \quad (5)$$

$$[b] = [(3 - R)/6][\mathfrak{L}_{(e-b)} + \mathfrak{L}_{(m-b)} + 2\mathfrak{L}_{(b-b)}] \quad (6)$$

where

$$R = 3[n] + 2[e] + [m] \quad (7)$$

and

$$[n] + [e] + [m] + [b] = 1 \quad (8)$$

Preliminary estimates of K_1 given in Table III were obtained from eq. 4, 5, 7, and 8.

For a system at equilibrium with respect to the sorting of building units into molecules, it can be shown that the equations presented in Table I correspond to the given fourth-order arrangements of building units about the bridges between units in the molecules, with the statistical sorting⁸ of the units being based on equal weighting of bonds. By use of an IBM-704 computer programmed to handle eq. 2, 3, 7, and 8, as well as the equations presented in Table I, the areas of peaks corresponding to various arrangements of building units around a linkage are readily obtained as a function of R for various assumed values of K_1 and K_2 . Such computations showed that for the first eleven values of R in Table II, the relative area of the $e-e$ resonance at -2.78 p.p.m. was essentially independent of the value of K_2 and that the best fit to the relative areas of this resonance in this composition range is given by $K_1 = 0.10$. With $K_1 = 0.10$ and $K_2 = 0.05$, a good fit was achieved with the three prominent peaks at -2.78 , -2.73 , and -2.91 p.p.m., for which a reasonably certain *a priori* assignment could be given. The other peaks appearing when $R > 1$ were then assigned by matching peak areas as a function of the R value (compare the calculated values in parentheses in Table II with the data).

While the value of K_1 quite certainly lies between 0.09 and 0.11, K_2 could not be established to lie within a smaller range of values than 0.1 to 0.001. The assignment of the most probable value of 0.05 to K_2 was based primarily on the fit of the $e-mm$ assignment to the resonance at -2.91 p.p.m. Thus, at $R = 1.44$, for example, 21.0, 23.9, and 28.1% of the total methylimino bridges were assigned to the $e-mm$ configuration for values of K_2 of 0.10, 0.05, and 0.001, respectively.

Since the data of Table II can be well fitted for R values between 3.0 and 1.6 (with a reasonably good fit all the way down to $R = 1.0$) without invoking the presence of ring structures, molecules based on rings

(7) *E.g.*, L. C. D. Groenweghe, J. H. Payne, and J. R. Van Wazer, *ibid.*, **82**, 5305 (1960); E. Schwarzmann and J. R. Van Wazer, *ibid.*, **82**, 6009 (1960).

(8) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); *ibid.*, **12**, 125 (1945). Also see J. R. Van Wazer, *J. Am. Chem. Soc.*, **72**, 644 (1950), and P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

TABLE II: OBSERVED PROTON NUCLEAR MAGNETIC RESONANCE PEAKS OF EQUILIBRATED COMPOSITIONS IN THE SYSTEM $AsF_3-As_2(NCH_3)_2$

| $R =$ F/As | Percentage of total methylimino bridges causing peaks at the chemical shift (in p.p.m.) shown ^a | | | | | | | | | | | | | | | | | | |
|---|--|-----------|-------|---------------------|-------|--------------------|--------------------|-------|---------------------|--------------------|---------------------|-------|--------------------|--------------------|--------------------|---------|-------|-------|--------------------|
| | -2.50 | -2.58 | -2.58 | -2.61 | -2.63 | -2.67 ^b | -2.73 ^b | -2.75 | -2.78 ^b | -2.80 | -2.83 ^b | -1.84 | -2.87 | -2.89 | -2.91 ^c | -2.95 | -2.98 | -3.02 | |
| 3.00 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| 2.77 | .. | .. | .. | .. | .. | .. | 9 | .. | 91 | .. | .. | .. | .. | .. | .. | .. | .. | .. | .. |
| | | | | | | | (9.6) ^d | | (89.5) ^d | | | | | (0.3) ^d | (0.5) ^d | | | | |
| 2.46 | .. | .. | .. | .. | .. | .. | 21 | .. | 74 | .. | .. | .. | .. | .. | 5 | .. | .. | .. | .. |
| | | | | | | | (22.0) | | (71.4) | (0.6) | (0.1) | | | (1.7) | (4.0) | | | | |
| 2.27 | .. | .. | .. | .. | .. | .. | 26 | .. | 57 | 5 | .. | .. | .. | .. | 11 | .. | .. | .. | .. |
| | | | | | | (0.1) | (27.3) | | (58.1) | (2.0) | (0.3) | | | (3.2) | (8.4) | | | | (0.1) |
| 2.11 | .. | .. | .. | .. | .. | 1 | 30 | .. | 37 | 10 | 2 | .. | .. | 3 | 17 | .. | .. | .. | .. |
| | | | | | | (0.2) | (29.1) | | (46.6) | (4.2) | (1.0) | | | (4.5) | (13.3) | | | | (0.2) |
| 2.00 | .. | .. | .. | .. | .. | 1 | 29 | .. | 41 | 8 | 2 | .. | .. | 3 | 16 | .. | .. | .. | .. |
| | | | | | | (0.4) | (28.4) | | (37.5) | (6.7) | (2.1) | | | (5.4) | (17.6) | | | | (0.4) |
| 1.93 | .. | .. | .. | .. | .. | 1 | 25 | .. | 32 | 12 | 5 | .. | .. | 4 | 21 | .. | .. | .. | .. |
| | | | | | | (0.6) | (27.0) | | (32.0) | (8.5) | (3.2) | | | (5.7) | (20.2) | | | | (0.6) |
| 1.71 | .. | .. | .. | .. | .. | 1 | 22 | .. | 24 | 17 | 6 | .. | .. | 5 | 26 | .. | .. | .. | .. |
| | | | | (0.9) | | (1.2) | (20.0) | | (18.2) | (13.9) | (8.9) | | | (5.5) | (25.5) | | | | (1.2) |
| 1.60 ^e | .. | .. | .. | .. | .. | 2 | 18 | .. | 20 | 16 | 9 | .. | .. | 7 | 27 | .. | .. | .. | 1 |
| | | | | (1.7) | | (1.7) | (15.3) | | (12.6) | (15.8) | (13.5) | | | (4.6) | (26.1) | | | | (1.7) |
| 1.44 ^f | .. | .. | .. | .. | .. | 2 | 18 | .. | 10 | 15 | 22 | .. | .. | 9 | 23 | .. | .. | .. | 1 |
| | | | | (3.9) | | (2.2) | (9.4) | | (7.0) | (16.0) | (20.4) | | | (3.2) | (23.9) | | | | (2.3) |
| 1.44 ^f | .. | .. | .. | .. | .. | 2 | 17 | .. | 9 | 15 | 23 | .. | .. | 9 | 24 | .. | .. | .. | 1 |
| | | | | (3.9) | | (2.2) | (9.4) | | (7.0) | (16.0) | (20.4) | | | (3.2) | (23.9) | | | | (2.3) |
| 1.34 | .. | .. | .. | 1 | .. | 2 | 15 | .. | 6 | 21 | 22 | .. | .. | 8 | 24 | .. | .. | .. | 1 |
| | | | | (6.2) | | (2.6) | (6.0) | | (4.3) | (14.4) | (24.5) | | | (2.1) | (20.5) | | | | (1.6) |
| 1.08 | .. | 2 | .. | 5 | 3 | 3 | 8 | .. | 17 | 17 | 18 | .. | 21 | .. | .. | .. | 6 | .. | .. |
| | | | | (13.7) ^g | | (2.7) ^g | (1.4) ^g | | (1.0) ^g | (7.0) ^g | (25.4) ^g | | (0.5) ^g | | (9.9) ^g | | | | (0.8) ^g |
| 0.81 | .. | 2 | .. | 10 | 4 | 4 | 9 | 12 | 17 | .. | 18 | .. | 15 | .. | .. | .. | 9 | .. | .. |
| | | | | (15.5) | | (1.6) | (0.2) | | (0.1) | (1.5) | (12.4) | | | (0.0) | (2.5) | | | | (0.5) |
| .65 | 1 | 1 | 2 | 10 | 3 | 2 | 7 | 12 | 10 | .. | 16 | 9 | 8 | .. | 5 | 6 | 8 | .. | .. |
| | | | | (11.2) | | (0.8) | (0.0) | | (0.0) | (0.4) | (5.4) | | | | (0.8) | | | | (0.2) |
| .56 | 1 | 1 | 2 | 8 | 2 | 2 | 4 | 17 | 6 | .. | 18 | 7 | 6 | 6 | 6 | 5 | 9 | .. | .. |
| | | | | (8.1) | | (0.5) | | | | (0.2) | (2.8) | | | | (0.4) | | | | (0.0) |
| .44 | 1 | .. | 1 | 4 | .. | 1 | 3 | 18 | 5 | .. | 20 | 8 | .. | 9 | 18 | 4 | 8 | .. | .. |
| | | | | (4.4) | | (0.2) | | | | (0.0) | (1.0) | | | | (0.1) | | | | |
| .23 | .. | .. | 1 | 1 | .. | .. | 1 | 8 | 2 | .. | 9 | 4 | .. | 12 | 49 | 7 | 6 | .. | .. |
| | | | | (0.7) | | (0.0) | | | | | (0.1) | | | | (0.0) | | | | |
| .00 | .. | .. | .. | .. | .. | .. | 1 | .. | .. | .. | .. | .. | .. | 20 | 78 | .. | .. | .. | 1 |
| Firm assignments for $R > 1$ | | | | | | | $e-me$ | | $e-e$ | $em-mm$ | $mm-mm$ | | | $em-me$ | $e-mm$ | | | | |
| Other reasonably certain assignments | | | | | | | $e-mb$ | | | | | | | b_b-b_b | b_4 cage for | | | | $em-mb$ |
| Tentative assign- ments | $e-b_b^m$ | $e-b_m^m$ | $b-b$ | $mm-mb$ | $b-m$ | | $mm-b_m^m$ | $b-b$ | Several $b-m$ | | $b-b$ | | $b-b$ | $b-m$ | | $bm-mb$ | $b-b$ | | |

^a For $R > 1$ and $R = 0$, the areas of the resonance peaks were measured, but for $0 < R < 1$, they were only approximated from the peak heights. ^b A slight upfield change (total = ca. 0.03 p.p.m.) was noted in the chemical shift of these peaks with decreasing R in the range of $1 < R < 3$. ^c As in b , but a downfield change. ^d Values in parentheses calculated for the firm assignments, using $K_1 = 0.10$ and $K_2 = 0.05$, from the theory of random sorting of building units into molecules (equal weighting of bonds), assuming no ring structures. ^e Data for $R > 1.6$ apply to both neat liquids and a 3:1 dilution with toluene; those for $R < 1.6$ apply only to the 3 toluene:1 sample solutions. ^f Typical replicate determination, starting from different batches of reagents. ^g For data below the gel point of $R = 1.12$, the theory underlying the calculated values becomes increasingly inapplicable as R decreases because of ring formation.

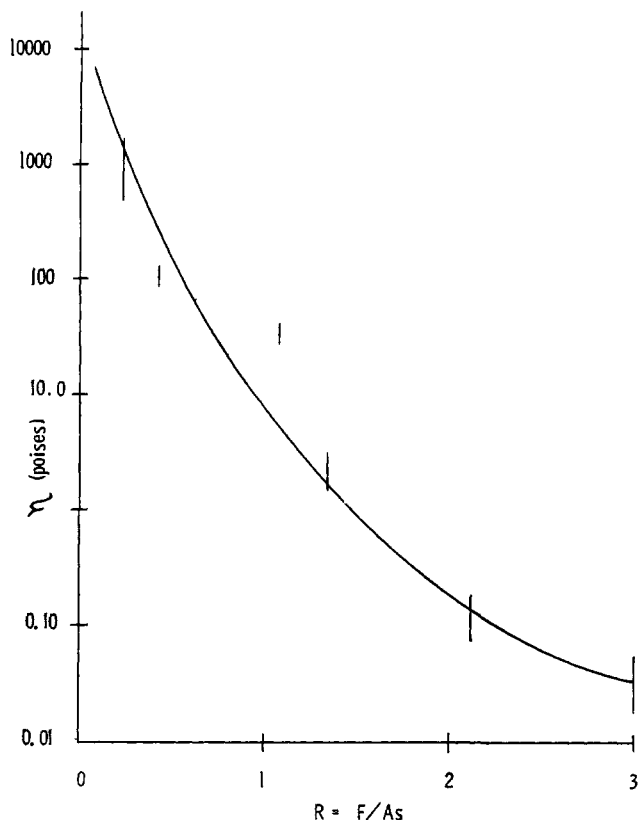


Fig. 2.—Variation of viscosity (plotted on a logarithmic scale) with composition at 25° for the system $\text{AsF}_3\text{-As}_2(\text{NCH}_3)_3$.

probably do not appear in the system in appreciable amounts at R values much greater than the one corresponding to the "gel point."⁸ For $K_1 = 0.10$ and $K_2 = 0.05$, the "gel point," assuming no rings, is found to lie at $R = 1.120$. For R values below the "gel point," there will necessarily be some rings but presently published theory is inadequate for their calculation and for estimation of the distribution of molecular species in this composition region. This means that data in the bottom third of Table II can only receive a qualitative interpretation.

TABLE III
PRELIMINARY ESTIMATES OF K_1

| R | K_1^a |
|------|----------|
| 2.77 | 0.09 |
| 2.46 | .08-0.10 |
| 2.27 | .10-0.13 |
| 2.11 | .17-0.23 |
| 2.00 | .08-0.11 |

^a The given range of values encompasses the various possible *a priori* assignments of the observed n.m.r. peaks.

Discontinuities and double maxima in the variation with R value of the intensity of a resonance appearing at a given chemical shift indicate that more than one structural arrangement must be assigned to that value of the chemical shift. This situation is found for peaks appearing at -2.78 , -2.83 , -2.89 , and -2.91 p.p.m. Furthermore, a systematic increase in the ratio of the observed to the calculated peak area of an assigned resonance indicates that, in the respective region of composition, two different arrangements of building units contribute to the resonance. Such a situation appears to hold for the resonance at -2.73 p.p.m. for $0.5 < R < 1.6$, and perhaps for those at -2.78 and -2.83 p.p.m. and for -2.89 p.p.m. in the range of $1.1 < R < 1.6$. This means that 24 arrangements of building units around a methylimino bridge

are resolved, as compared to the possible 55 arrangements corresponding to a second-order bridge environment plus any additional resonances due to ring structures, including cage compounds. Since the n.m.r. data for R values below the "gel point" were obtained for a threefold dilution with toluene, formation of ring structures will be promoted if, as indicated below, the rate of rearrangement of building units is sufficiently rapid so as to allow equilibration to be achieved nearly immediately after dilution. Some suggestions as to the assignment of n.m.r. peaks for R values below the "gel point" are presented in the last two columns of Table II. Toluene solutions of the carefully recrystallized cage compound, $\text{As}_4(\text{NCH}_3)_6$, gave a principal sharp resonance peak at -2.91 p.p.m. (96%) as well as a minor peak at -2.83 p.p.m. (4%). When samples of this material were heated in sealed glass tubes under nitrogen for several hours at 130°, homogeneous liquids resulted which, after fairly rapid cooling to room temperature, formed a solid mass containing some $\text{As}_4(\text{NCH}_3)_6$ crystals. This material dissolved in toluene to give a limpid liquid but complete dissolution was not effected in less than 12 hr. The proton n.m.r. spectra of such toluene solutions exhibited two major, sharp resonances and two minor ones, as shown in the last line of data in Table II. The resonance seen at -2.88 p.p.m. for low values of R is undoubtedly attributable to the $\begin{smallmatrix} b \\ b \end{smallmatrix} b - \begin{smallmatrix} b \\ b \end{smallmatrix} b$ arrangement in structures other than the $\text{As}_4(\text{NCH}_3)_6$ bird-cage molecule.

Group-Transport Phenomena.—The fact that the F^{19} spectra showed only a single broad peak for either the neat liquids or toluene solutions of compositions having R values greater than unity shows that the rate of exchange of fluorine atoms between chemically different sites is a rapid process in this region of composition. Since this resonance peak shifts upfield and broadens greatly with decreasing R , one must conclude that it represents a coalescence of a number of resonances corresponding to different arrangements of building units, with the peaks due to end units appearing around -17 p.p.m., those due to middle units in chains around $+5$ p.p.m., and those attributable to middle units in fused(?) rings perhaps having as positive a chemical shift as $+20$ p.p.m.

The separate, rather sharp resonance peaks seen in threefold dilutions with toluene and denoted in Fig. 1 by crosses are probably attributed to arrangements of middle groups with branches in relatively small molecules, including cage structures. From the line widths of these peaks and the shapes of the low saddles between certain neighboring pairs of them, a lifetime for fluorine in a given atomic arrangement may be estimated.⁹ A number of calculations based on the ten peaks shown as crosses in Fig. 1 gave a consistent value of $(3 \text{ to } 4) \times 10^{-3}$ sec. for this lifetime. Similar treatment of the line widths of the prominent resonances in the proton spectra of the low-viscosity neat liquids corresponding to $1.9 < R < 2.8$ again gave a narrow range of lifetimes for exchange of hydrogens between chemically different sites, this time clustering around 0.1 to 0.2 sec. Since hydrogens on methyl groups are known not to exchange rapidly at room temperature and since the same is true of methyl groups on nitrogen, the observed lifetime of 0.1–0.2 sec. corresponds to shifting of $\text{CH}_3\text{N}<$ bridges through the making and breaking of As–N bonds.

As shown in Fig. 2, the viscosity of freshly prepared equilibrated neat liquids in the system $\text{AsF}_3\text{-As}_2\text{-}$

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y. 1959, pp. 220–225.

(NCH_3)₃ increases with decreasing R value, going from a limpid liquid at $R = 3$ to an extremely viscous, nearly solid, homogeneous, transparent mass at $R = 0.23$. This means that the neat liquids flow at R values below the "gel point" calculated from fitting the proton n.m.r. data of Table II to the statistical theory of ring-free molecules at equilibrium with respect to exchange of their parts. Of course, the presence of ring structures, including cages based on fused rings, can shift the "gel point" in the extreme case to $R = 0$. However, it is expected that the presence of a moderately large fraction of the total As in ring structures at $R = 1.12$ would lead to amounts at higher R values sufficiently large so as to spoil the fit between experiment and theory in Table II. An alternative explanation for flow beyond the "gel point" corresponding to no rings in the finite molecules would be a sufficiently rapid making and breaking of As-N bonds in the network structure to permit flow by this mechanism. Presumably the "gel point" appears at a somewhat lower R value than presented above for a ring-free system and the observed flow is due in part to the making and breaking of chemical bonds holding the parts of the molecules together.

Conclusions

As was found in the case of the polyarsenous oxyfluorides¹⁰—which form a family of compounds similar to the one described herein except that the arsenic atoms are linked together in the molecules by oxygens rather than methylimino bridges, the poly(fluoroarsenous methylimides) consist of labile molecules which exchange parts with each other so rapidly at room temperature that they would be impossible to separate by standard methods. However, unlike the $\text{AsF}_3\text{-As}_2\text{O}_3$ system,¹⁰ which corresponds to nearly

(10) J. R. Van Wazer, K. Moedritzer, and D. W. Matula, *J. Am. Chem. Soc.*, **86**, 807 (1963).

random sorting, the end and middle groups are present in much greater amounts than randomly expected in the system $\text{AsF}_3\text{-As}_2(\text{NCH}_3)_3$. This means that an appreciable energy is associated with the exchange of methylimino bridges for fluorine atoms on an arsenic, and this may be explained in terms of nonbonding interactions arising from electron correlation.¹¹ Such nonrandom behavior is in accord with our findings on exchange of dimethylamino groups with halogens in *meso* compounds based on a single arsenic,² phosphorus,¹² germanium,¹³ or silicon atom.¹⁴

When the values of the equilibrium constants relating structure-building units are considerably smaller than their random values, as in the case of the family of compounds studied here ($K_1 = 0.10$ and $K_2 = 0.05$ as compared to $K_{\text{rand}} = 0.33$), straight-chain oligomers are produced when the ring-chain equilibria are shifted toward the chains, as has been found to be true in this case. Thus, for $R = 1.125$, we calculate that 70% of the molecules and 20% of the total arsenic are present in unbranched-chain molecules, with 5% of the total arsenic in straight chains having 10 or more arsenic atoms in their structure. This paper exemplifies the fact that the study of deviations from random sorting of substituents in scrambling reactions of simple compounds may be employed to predict the structural properties of a previously unknown family of compounds of sufficient lability so that the preparative operations lead to full or partial equilibration with respect to exchange of parts between the molecules. A general theoretical treatment of such systems is underway in our laboratory.

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(14) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 268 (1964).

[CONTRIBUTION FROM THE INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY, UNIVERSITY OF FLORENCE, FLORENCE, ITALY]

Investigation on the Occurrence of Tetrahedral Forms of Substituted Bis(N-alkylsalicylaldimino)nickel(II) Complexes¹

BY L. SACCONI, M. CIAMPOLINI, AND N. NARDI

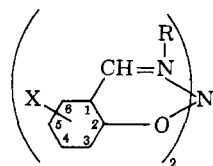
RECEIVED OCTOBER 1, 1963

Spectrophotometric, magnetic, osmotic, and dielectric polarization measurements on three series of ring-substituted R-N-salicylaldimino-nickel(II) complexes ($R = n$ -propyl, *sec*-alkyl, *t*-butyl) have been made. In the solid state the *n*-propyl derivatives are planar, the *t*-butyl derivatives pseudo-tetrahedral. The *sec*-alkyl complexes are either planar or pseudo-tetrahedral depending on the nature and position of the ring substituent. In inert solvents at room temperature the *n*-propyl derivatives are essentially planar, the *t*-butyl derivatives largely pseudo-tetrahedral; the *sec*-alkyl complexes generally exist in comparable proportions of either forms. The proportion of the tetrahedral form in the *n*- and isopropyl complexes increases with increasing temperature; the opposite occurs in the *t*-butyl derivatives. The enthalpy and entropy changes were calculated from the temperature dependence of the constant for the equilibrium between planar and tetrahedral allomers. The results are discussed in terms of electronic factors and steric requirements of the ligand groups.

Introduction

We have recently shown that the paramagnetism of many N-*sec*-alkyl,² N-*n*-alkyl,³ and N-arylsalicylaldiminonickel(II)⁴ complexes is often due to a tetrahedral structure, both in the solid state and in solution; an X-ray structural investigation then showed unambiguously that the isopropyl derivative has the tetra-

hedral configuration.⁵ With the aim of studying the factors which influence the occurrence of such a structure we prepared some series of nickel(II) complexes with ring-substituted N-alkylsalicylaldimines of the general formula



(1) This research was supported by the U. S. Department of the Army through its European Research Office, under Contract No. DA-91-591-EUC-2965, and by the Italian "Consiglio Nazionale delle Ricerche."

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