Journal of Organometallic Chemistry, 102 (1975) 445—455

(HALOMETHYL)ARSENIC COMPOUNDS

II*. PREPARATION AND DYNAMIC NMR SPECTRA OF PENTAKIS(CHLOROMETHYL)CYCLOPENTAARSINE

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(Received April 10th, 1975)

Summary

Hypophosphorous acid reduction of chloromethylarsonic acid produces the novel cyclopolyarsine, pentakis(chloromethyl)cyclopentaarsine (PCCA). PCCA possesses a greater thermal and oxidative stability than other cyclopolyarsines previously studied. The dynamic PMR properties of PCCA are interpreted as a combination of a low-energy limited pseudorotational motion and a higher-energy As-atom inversional process. An alternative to ground-state *d*-orbital participation in the interpretation of the electronic spectra is offered.

Introduction

It was recognized early in the history of organoarsenic chemistry that products containing As—As bonds were common terminations of reactions involving mono- and diorganoarsenic reagents. With diorganoarsenic reagents the terminal products are diarsines, R_2AsAsR_2; with monoorgano reagents, the possibility for a great variety of oligomers (usually cyclic) and polymers (chains and ladders) exist, all characterized by the empirical formula RAs [1-3]. Cyclic oligomers, $(RAs)_n$ where R = alkyl, aryl, silyl or germyl and $n = 4$ to 6, possess puckered rings of As atoms, and especially when R = alkyl, appear to have a single, preferred value of n for each R group. All primary alkyl-substituted cyclo-

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* For Part I, see ref. 7.

polyarsines are pentamers $(RAs)_5$, and all secondary and tertiary alkyl-substituted cyclopolyarsines are tetramers $(RAs)_4$ [3].

This paper describes the preparation and physical characterization of a new cyclic oligomer, pentakis(chloromethyl)cyclopentaarsine (PCCA)*, of interest because of the presence of both a sterically demanding and electron withdrawing substituent. Nixon reports [4] that one of the products of the decomposition of $ClCH_2PF_2$ under mild conditions is a not well-characterized yellow liquid believed to be a cyclic polyphosphine, $(ClCH_2P)_n$, with n most likely five [5].

Experimental

PMCA was prepared by the hypophosphorous acid reduction of sodium methylarsonate [6] but was not distilled before use. Chloromethylarsonic acid, prepared as previously described [7], was reduced in aqueous solution by 50% hypophosphorous acid to the cyclic oligomer PCCA by essentially the same procedure as used for PMCA. PCCA separated as an intensely yellow, heavy oil of undetermined boiling point which was purified by repeated 5% $NaHCO_3$ and water washings followed by a 2 h degassing at 10^{-4} mmHg, but was not distilled. Previous experience has shown that PMCA undergoes partial, irreversible and not well understood changes on mild heating, e.g., during distillation [8,9]. PCCA is soluble in both benzene and ether, and insoluble in water. (Found: C, 9.72; H, 1.65; Cl, 28.28. CH_2AsCl calcd.: C, 9.66; H, 1.62; Cl, 28.49%.)

The susceptibility of PCCA to aerobic oxidation is undetectable, as compared to PMCA, which in thin films is pyrophoric. Additionally, no arsine-like odor is found surrounding exposed samples. PMCA often forms solid red-brown modifications on standing which when heated to 180°C revert to its original state [9]. Purified PCCA, however, showed no tendency to produce solid forms even after a 20-day exposure to humid air. During its preparation PCCA did form red-brown solids which could not be thermally restored to a liquid state even when heated to 300°C in an evacuated tube.

The pentameric nature of the product was deduced from its PMR spectrum which according to whether it was measured neat or in solution displayed peaks in integrated ratios of either 2/3 or 2/2/1, and was confirmed by its osmometric molecular weight: found, 589, calcd. 612. Considerable difficulty was experienced in obtaining a satisfactory mass spectrum of PCCA attributable to its extreme involatility. Samples of PCCA heated to 260°C under nitrogen showed no evidence of thermal decomposition; PMCA decomposes irreversibly at 205°C.

The NMR spectra were recorded on either a Varian A-60D or a Perkin—Elmer R20B spectrometer each equipped with their manufacturer's variable temperature controller; UV spectra were recorded on a Cary 14 spectrometer.

Viscosity measurements on PMCA were obtained by the falling sphere method using a 1.52 mm radius steel sphere in a 4 × 150 mm glass tube. The tube was filled to capacity and sealed with an epoxy cement plug. Fall times were used directly without compensation for changing ball or fluid den-

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* PCCA = pentakis(chloromethyl)cyclopentaarsine, $(ClCH_2As)_5$; PMCA = pentamethylcyclopentaarsine, $(CH_3As)_5$; PFCA = pentakis(trifluoromethyl)cyclopentaarsine, $(CF_3As)_5$; and PECA = pentaethylcyclopentaarsine, $(CH_3CH_2As)_5$.

sities in the viscosity computations, but were calibrated by known viscosities of common fluids. The tube was immersed in an insulated oil bath and inverted by means of an external crank handle. Temperature measurement errors were estimated to be ±2°C and time errors to be not more than ±5%.

Results and discussion

Structural data on pentameric cyclopolyarsines are limited to the methyl derivative. Both electron [9] and X-ray diffraction [10] studies support the presence of a puckered five-membered ring. The absence of symmetry in the crystallographic structure (Fig. 1a) dictates that each methyl group is unique and that, if the solid-state structure persists in solution, the NMR spectrum should consist of five equal-intensity lines. All spectra of cyclopentaarsines show three or fewer lines; even the ^{19}F NMR spectrum of PFCA, where chemical shift differences are large and the likelihood of accidental degeneracies small, displays only a three-line pattern of intensity ratio 2/2/1 [11]. Furthermore, five-line spectra have not been observed for either PMCA or PFCA even when cooled to −100°C [11]. For PCCA, depending upon solvent, dilution, and temperature, spectra always show either a 2/2/1 or 2/3 pattern.

One is forced, therefore, to propose a means by which cyclopentaarsines obtain either a permanent or time-averaged plane of symmetry (Fig. 1b). The phenomenon responsible for these effects is likely one of five possibilities: (1) As-atom inversion, (2) ring opening—closing equilibria in which pentameric forms are retained, (3) ring opening—closing equilibria involving alteration in oligomer size, (4) cyclopentane-like pseudorotation, and (5) that the asymmetrical solid-state structure results from crystal packing requirements which relax in solution

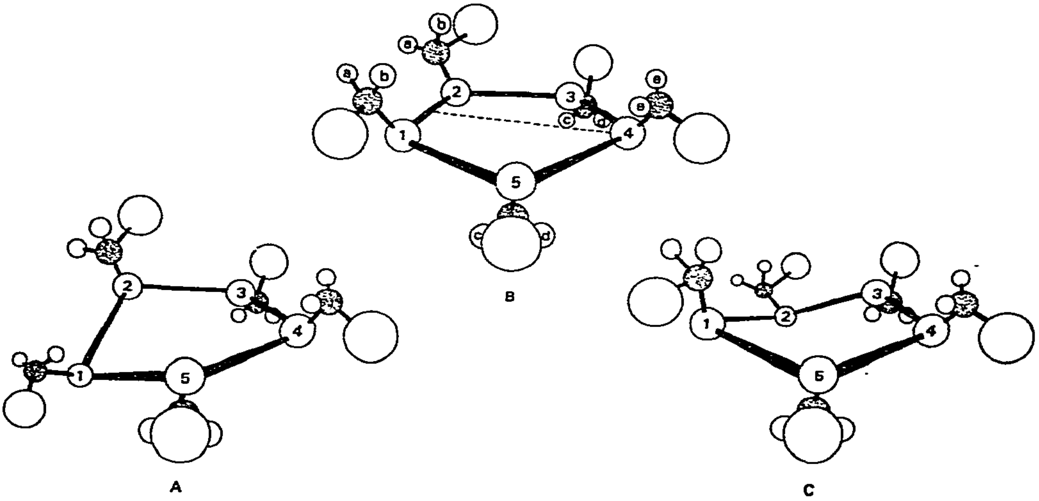

Fig. 1. A schematic depiction of a torsional (restricted pseudorotational) motion of $(ClCH_2As)_5$ along the As(1)—As(2) bond which converts structure A into its mirror image, structure C, through the symmetrical intermediate, structure B (– – – represents the intersection of a vertical plane of symmetry). Structures A and C derive from the crystallographic structure of $(CH_3As)_5$ [10]. The lower case letters in structure B designate isochronous pairs of protons.

(a non-fluxional interpretation). The fluxional options (1-4) require that the symmetry generating motion be rapid, even at very low temperatures, and thus be characterized by a low activational free energy.

Although Lambert has shown that inversion of As atoms in diarsines is more rapid than inversion in monoarsines (due perhaps to the stabilization of planar intermediates through a maximization of p_π—d_π interactions) [12], reasonable estimates for minimal activational barriers for As-atom inversion are likely not less than 80-85 kJ mol^{-1} [13], a barrier seemingly unsurmountable at —100°C especially since a symmetry-generating motion would be expected to be accompanied by a negative activational entropy. $\Delta G^{\neq}$ (—100°C) for the symmetry generating motion can be approximated from chemical shift data as being not greater than 25-30 kJ mol^{-1}. In view of this, a recently proposed wag-inversion mechanism [11] must be viewed with skepticism. Furthermore, Mislow has also demonstrated that inversion barriers in phosphines (including diphosphines) can be correlated with substituent electronegatives: the greater the electronegativity the higher the barrier [13,14]. Inversion processes may, however, be responsible for a different, high-temperature dynamic behavior described later.

All ring opening—closing equilibria necessitate As—As bond cleavage, but may be facilitated by impurities introduced either during preparation or through thermolytic or photolytic decomposition of pure cyclopolyarsine. Examples of sample-history dependent phenomena are known [8]. Again, however, although possibly relevant at elevated temperatures, ring opening equilibria whether catalyzed or not, require not only the expenditure of the As—As bond dissociation energy (ca. 150 kJ mol^{-1}), but also the loss of the difficulty estimated stabilization achieved through transannular, non-bonded As—As interactions*. If the interpretation that weak up-field lines seen in PMCA NMR spectra are due to *catena* species is correct [8,11], then the absence of temperature-dependent spectral features for the weak lines (up to 180°C) suggests that a *cyclo—catena* equilibrium is not the low-temperature dynamic process responsible for the generation of symmetry. Additionally, the linearity of the viscosity data reported below suggests that the ring remains intact between 25 and 190°C.

Most attractive of the alternatives appears to be a cyclopentane-like pseudorotation [15], a rotation of the position of maximum puckering in stepwise, random, or alternate exchange (between two favored positions) patterns resolvable into vertical motions of As atoms. Pseudorotation of unspecified pattern was first suggested by West and coworkers [8] as an explanation for these low-energy fluxional processes**. Unlike inversion, pseudorotation preserves the non-equivalency of As atoms. Differences must therefore exist in the barriers for specific pseudorotational transitions (both 1,2 and 1,3 exchanges are possible). Pseudorotation need not occur at all As atoms with equal frequency, i.e., the differences between the bottoms and saddle points on a five-well, free-energy

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* It is difficult to account for the remarkable thermal stability of cyclopolyarsines compared to *catena*-polyarsines unless additional sources of stabilization, e.g., transannular attractive interactions, are proposed.

** Wells et al. [11] have proposed that the high-temperature NMR phenomena described elsewhere in this paper are attributable to a stepwise pseudorotation.

annulus will differ at each position. The simplest (and therefore probably least energy) pseudorotational motion capable of generating the required symmetry would be one that made the 1 and 2 positions equivalent and transferred the puckered position to 4 (see Fig. 1) followed by a return of puckering to either position 1 or 2. Note that motion at position 4 is not a requirement; a simple torsional motion along the As(1)—As(2) axis suffices.

The general features of the solid-state structure of PMCA also pertain to those cyclopentaphosphines whose structures have been determined [16]. It is reasonable, therefore, to conclude that the favored ring conformation in solution phases closely resembles the solid-state structure, a structure preferred for its minimization of repulsive electronic and steric interactions and not the result of crystal packing requirements.

The PMR spectrum of PCCA would be expected to be more complex than that of PMCA. In the absence of a symmetry generating motion, not only are the chloromethyl groups anisochronous, but so also are the two protons of each group, producing (in theory) five, distinct *AB* spin patterns (presuming that coupling between adjacent chloromethyl groups is negligibly small). In the presence of the proposed symmetry-generating torsional motion, the spectrum would reduce to two distinct *AB* patterns, the protons on C(1) and C(2) producing degenerate *AB* patterns, likewise C(3) and C(5) and a single line for the isochronous protons on C(4). As $J(AB)/\Delta\nu(AB)$ becomes large (>1.0), the appearance of an *AB* pattern collapses to a closely-spaced central doublet as the outer lines fade in intensity, and as $\Delta\nu(AB)$ approaches zero, all lines collapse to a singlet. It is reasonable to expect that the values of $\nu(A)$ and $\nu(B)$ will differ only very slightly.

As a 20% (by weight) solution in chlorobenzene, PCCA shows a narrow line-width (<1.0 Hz at half height) three-line spectra in a 2/2/1 intensity ratio at τ 5.91, 6.05 and 6.06. The two closely spaced high-field peaks merge at similar dilution in benzene and toluene. Since the line with a relative intensity of one must represent the $ClCH_2$ group on As(4) and since the $ClCH_2$ environments for positions 3 and 5 resemble 4 more than 1 or 2, the τ 5.91 line is assigned to the 1, 2 pair and the τ 6.05 line to the 3, 5 pair.

At room temperature and below, spectra of neat PCCA are badly viscosity broadened as seen also in PMCA, but at 42°C show the same three-line spectrum found in chlorobenzene (Fig. 2). Two smaller peaks (totaling about 10% of the intensity of the main peaks) appear upfield at τ 6.22 and 6.25. The presence, position and intensity of the weaker peaks are not a function of sample history or its method of preparation, and must therefore, be due to species derived from, and in equilibrium with, PCCA. The weak upfield may represent catena species, but, if this is the case, then the *cyclo—catena* equilibrium conversion rate must be slow on the NMR time scale as temperature effects are not seen for these lines. Similar weak upfield peaks are found in neat samples of PMCA and similar arguments have been applied to their origin [8,11].

The NMR spectra of PCCA lead, therefore, to the conclusion that the chemical shift difference between geminal protons at positions 1, 2, 3 and 5 must be unobservably small, i.e., the anticipated *AB* quartet patterns have collapsed to singlets. A 100 MHz NMR spectrum of PECA has been published by West and coworkers [8]. At 120°C where all viscosity broadening has disappeared, these

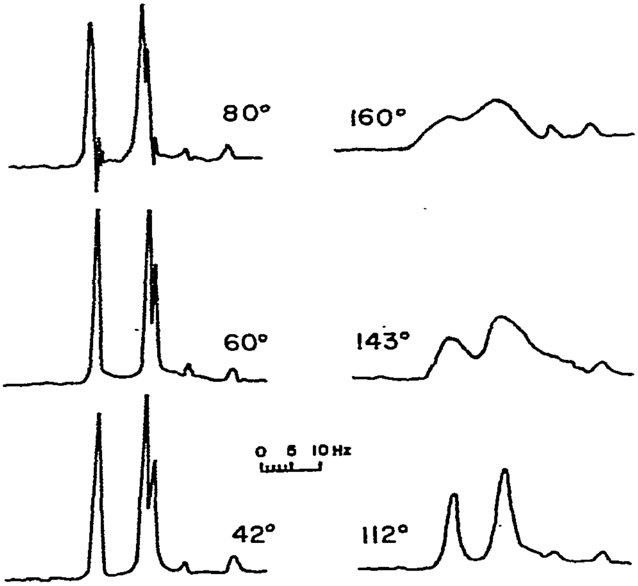

Fig. 2. Variable-temperature 60 MHz spectra of $(ClCH_2As)_5$.

authors find a spectrum of high complexity, deriving, they suggest, from slow pseudorotation producing non-equivalency among all ethyl groups. If the suggestion of West et al. is accepted, the conclusion must be that PMCA pseudorotates NMR rapidly at —100°C while PECA does so only slowly at +120°C; a 220°C temperature difference for these essentially isoentropic processes appears unreasonable. Clearly, however, the methylene portion of the ethyl group should, at least in theory, also contain anisochronous protons and produce, in the presence of NMR-fast pseudorotation, one A_2B_3 and two ABC_3 patterns (which could be indistinguishable from A_2B_3 patterns if $\Delta\nu(AB)$ is small). In fact, the spectrum of West et al. looks more like overlapping A_2B_3 patterns where $J(AB)/\Delta\nu(AB)$ is about 0.1; the anticipated vicinal constant for a freely rotating ethyl group is about 7 Hz and the PECA spectrum appears to have a $\Delta\nu$ of about 75 Hz. Thus if, as in PCCA, the chemical shift difference between geminal (CH_2) protons is unobservably small, the spectrum of West et al. is reasonable for three overlapping A_2B_3 patterns, not five triplet—quartet (first-order ethyl) patterns.

When PMCA is heated above 160°C complex, often poorly reproducible, and sometimes sample history dependent phenomena occur [8]. Wells et al. [11] report that the NMR multiline spectra of PMCA and PFCA collapse reversibly to single lines; above about 170°C the lines broaden again continuously to the highest temperature observed, 200°C. In the range of 170-200°C the smaller upfield lines also broaden and eventually disappear. West et al., however, find no loss of triplet structure or alteration in the upfield peaks when fresh samples of PMCA are heated to 178°C, but does find the previously reported broadening and collapse of all lines when samples have been preheated at 190°C for 2 h [8]. They found that preheated samples of PMCA contained a high mass spectral abundance of $(CH_3)_4As_2^+$ ions at m/e 210 that were absent in unheated samples.

Our own experience with PMCA resembles that of Wells et al. [11]; although no m/e 210 ions were found in our samples, coalescence was achieved at about the same temperature they observed. Samples of PMCA that were thoroughly degassed or left undegassed, samples purposely poorly washed to leave residues of excess hypophosphorous acid or carefully and repeatedly washed, samples distilled or crude, all showed coalescence at ±3°C of the temperature reported by Wells et al.*. The exposure to normal laboratory fluorescent illumination did, however, produce significant changes; after one week, exposed samples of highly refined PMCA showed a coalescence temperature 10°C below the temperature reported by West et al. [8]. They do not report if this preheating occurred in light or darkness.

Variable-temperature NMR spectra of PCCA (Fig. 2) show a gradual increase in line broadening between 80°C and 160°C, but this is not accompanied by a substantial change in either the "shape" of the spectral envelope for the major set of absorptions or in the relative intensities or linewidths of the weaker, upfield lines. The retention of general line envelope throughout the temperature range studied could argue against a process involving As-atom inversion which would create ring forms (see Fig. 3) with increased non-bonding electron pair repulsions and different $ClCH_2$-group chemical shifts causing distortion of the absorption envelope. If puckering is, however, retained in these higher energy invertomeric structures, each would, at least in theory, still produce three-line spectra of 2/2/1 relative intensity. We are not suggesting that the line-broadening phenomenon is the result of dynamical averaging of these invertomeric forms, but rather that as the temperature is increased the equilibrium concentration of less favorable forms is increased. Because of the close similarity of chemical shifts anticipated among the invertomeric forms, broadening occurs through the spectrometer's inability to resolve the individual lines. At these elevated temperatures, As-atom inversional barriers for PCCA can be realistically surmounted. In this regard, Lambert et al. have found that As-atom inversion in diarsines becomes NMR-rapid at about 180°C [12]; at 180°C coalescence of the methyl resonances for the *d, l* and *meso* forms of 1,2-dimethyl-1,2-diphenyl diarsine is achieved through inversion (coupled with As—As bond rotation). Mislow and coworkers [13] suggest that the coalescence process may be intermolecular. This suggestion has received recent support from a restudy [18] of dynamic

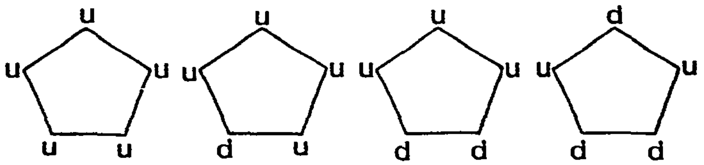

Fig. 3. Four possible inversional isomers for a five-membered ring of arsenic atoms based upon the up ("u")—down("d") relationship of non-bonding pairs (or substituents). The isomers are intuitively arranged in order of decreasing internal energy (from left to right) by consideration of non-bonding pair interactions.

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* Unrefined samples did show much more rapid formation of polymeric red-brown *catena*-polymethylpolyarsine than found in refined samples.

processes in diphosphines. The restudy was conducted in CH_2Cl_2, the original in biphenyl; the difference in solvent polarities may account for this apparent conflict in results.

Contrary to the observations for PMCA [8,11], however, the high-temperature behavior of PCCA is not rapidly reversible; the broadened, two-line spectrum of neat PCCA at 160°C does not fully revert to its room temperature spectrum until 24 to 30 h have elapsed. Since all other cyclopentaarsines so far studied rapidly (as fast as samples can be cooled in the spectrometer, ~20°C/min) equilibrate on cooling, only the steric bulk of the $ClCH_2$ groups in PCCA can account for the retarded rates of reequilibration. On cooling, PMCA rapidly reverts to its thermal ground state, but PCCA may be "frozen out" in thermally excited invertomeric forms, i.e., PCCA readily supercools. The higher barrier to interconversion of invertomeric forms for PCCA must derive from crowding imposed by the sterically demanding chlorine atom. Each inversion requires a simultaneous C—As bond rotation to accommodate sterically the Cl atom (convincingly seen from space-filling models), but such rotations are restricted by the severe interaction of the Cl atom with the As atoms three bonds removed. These steric entanglements could prevent rapid return to a thermal ground state. Concentration dependency studies in t-butylbenzene indicate that the rate of return to ground state is an intramolecular process.

As an alternative to an explanation requiring sterically entangled invertomeric forms, ring-opening—ring-closing equilibria producing zwitterion or diradical intermediates may be involved. The first explanation involves an intramolecular process and should not significantly effect the viscosity while the alternative would be expected to produce anomalous viscosity behavior.

We have obtained variable temperature viscosity data for PMCA between 25 and 190°C by the falling sphere technique (too small a quantity of PCCA existed for comparison measurements). In the temperature range investigated, we find a linear relationship (within experimental error) between log viscosity and T^{-1} with an activation energy for flow of 18.5 kJ mol^{-1}* (Fig. 4), and an extrapolated "frequency factor" of 2.5×10^{-4} (a typical value for an unassociated liquid). The phenomenon in question, therefore, must be intramolecular (e.g., inversion) and cannot be a ring-opening—ring-closing equilibrium which would, by analogy to liquid sulfur [20], lead to nonlinear viscosity/temperature behavior. We have no reason to believe that the conclusions drawn from these viscosity data are not also applicable to other cyclopolyarsines.

PCCA exhibits several other properties that differentiate it from other cycloarsines. It is, for instance, indefinitely stable in contact with humid air, whereas PMCA is pyrophoric, and PFCA is rapidly hydrolyzed at room temperature [8]. Consistent with its stability to oxidation and hydrolysis is our finding that PCCA possesses the longest wavelength UV absorption of any cycloarsine reported, λ_{max} 350 nm, as compared to 300 nm for PMCA when measured as 10^{-3} *M* solutions in benzene. This UV transition is attributed by many to a lone-pair delocalization into an empty *d* level or other orbital of suitable sym-

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* Van Wazer, et al. have reported an activation energy of about 33 kJ mol^{-1} [17]. The empirical observation that the ratio of the heat of vaporation (ca. 63 kJ mol^{-1} for PMCA [9]) to the activation energy is between 3 and 4 [19] suggests that the earlier reported value may be too high.

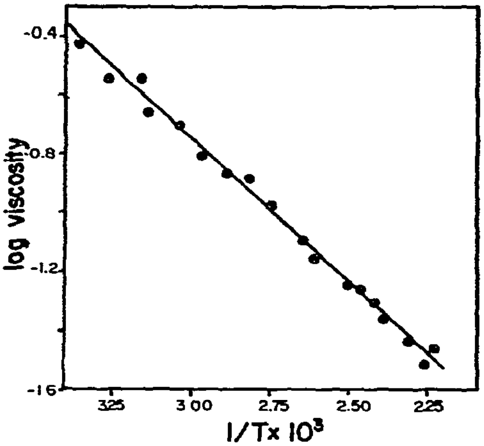

Fig. 4. Plot of log viscosity (poises) and reciprocal temperature (K) for PMCA.

metry on an adjacent arsenic atom [21]. There is great difficulty, however, in extending this argument to a picture of circumannular delocalization in the classical aromatic sense. A molecular orbital constructed from *p* and *d* orbitals cannot produce conjugation in a non-planar structure via p_π—d_π bonding.

An alternative to ground-state *d*-orbital involvement can be proposed. Two filled molecular orbitals constructed of *s* and *p* atomic orbitals, e.g., two non-bonding electron pairs on adjacent As atoms, can interact to an extent determined by their dihedral angle (along the As—As bond axis) reaching a maximum at an angle of 0°. Although the total energy of such a system remains constant with variation in dihedral angle (if secondary effects are neglected), the HOMO [22] does increase in energy thus lowering the HOMO—LUMO separation, Fig. 5. Similar molecular-orbital descriptions have been used effectively by Weiss [23] in the analysis of charge-transfer spectra of disulfides and by Cowley, Dewar et al. [22] in a photoelectron-spectroscopy study of CF_3-substituted cyclotetra- and cyclopenta-phosphines. Cowly, Dewar et al. find evidence not only for 1,2 lone-pair interaction but also for transannular interaction*. Other aspects of their data strongly support the position that p_π—d_π bonding is relatively unimportant in phosphorus—phosphorus bonding; one can safely assume the extendibility of these results to arsenic—arsenic bonding as well. If, by analogy to cyclopolysilanes [24,25], the LUMO for cyclopolyarsines is largely *d* in character, some excited state delocalization appears likely.

It is important to note that the lowest energy absorption in cyclopenta-

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* It should be pointed out that in their study Cowley, Dewar et al. [22] found evidence for lone-pair interactions in $(CF_3P)_4$ but not $(CF_3P)_5$. This they attribute to the absence of symmetry in the pentamer but give reference only to a solid-state structural determination. In solution, however, Wells et al. [11] has found, as is true also for other cyclopentamers, that at least C_s symmetry is achieved permitting symmetry-allowed lone-pair orbital interactions. This leads to three presently unresolvable interpretations: (1) cyclopentamers revert to an asymmetric structure in the vapor state (required for photoelectron spectroscopy), (2) fluxional motions which create the C_s symmetry prevent orbital association (unlikely considering the vast difference in time scales), and (3) that Cowley and Dewar's interpretation of their spectra is incorrect.

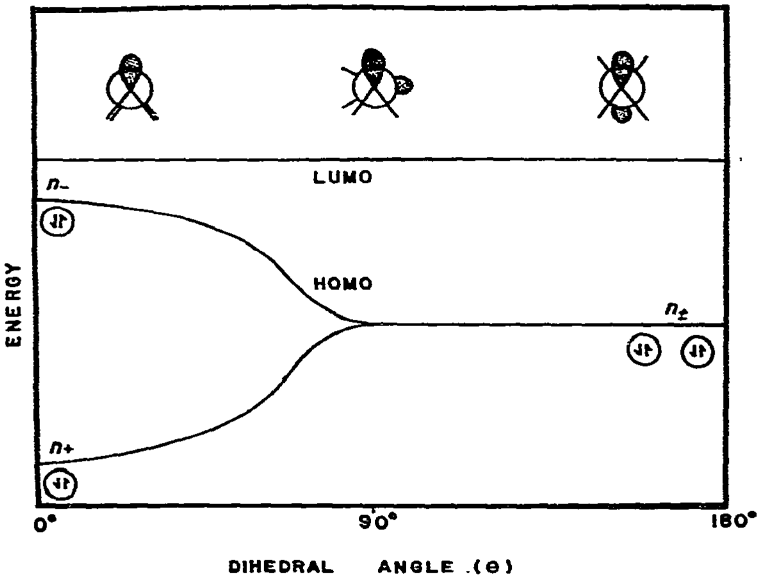

Fig. 5. The variation of the HOMO—LUMO separation as a function of the dihedral angle (ϕ) relating non-bonding pairs on adjacent arsenic atoms. The interaction of electron pairs, while a cos (ϕ) function of the dihedral angle, need not fall to zero at 90°.

arsines (and phosphines) is considerably red-shifted compared to either cyclotetra- or cyclohexa-arsines [21,26], and that it is only the cyclopentamers that require a time-average structure with a 0° (or near 0°) dihedral angle between two adjacent lone-pairs.

The steric restrictions imposed by the $ClCH_2$ groups may have a dampening effect on pseudorotation (or a limited pseudorotation such as the torsional motion earlier described) thus restraining the oscillations to a narrower region either side of a 0° dihedral angle.

In bis[*catena*-poly(methylarsenic)](BCPA), a high-molecular-weight ladder polymer constructed of CH_3-substituted As atoms [2], all non-bonding electron pairs along a ladder upright are constrained to a nearly 0° dihedral angle relationship. BCPA is intensely puprple, λ_{max} ca. 450 nm and shows the electrical properties of an intrinsic semiconductor with an energy gap of about 1.3 eV. Ac conductivity measurements strongly indicate a "hopping" mechanism for electron mobility at 25°C [27] suggesting that extended excited-state delocalization in this (and perhaps all) polyarsines is unimportant in confirmation of the electrochemical results of West et al. [24a]*.

Acknowledgements

This research project was in part supported by the Office of Naval Research. The viscosity measurements were obtained by E.J. Pleau.

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* West has recently reported [24b] his inability to prepare either chemically or electrochemically radical anions from cyclopolyphosphines; he interprets these negative results as an indication of a reduced *d*-orbital LUMO stabilization for cyclopolyphosphines as compared to cyclopolysilanes.

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