# STEREOCHEMISTRY OF 2-SUBSTITUTED 5,6-BENZO-1,3,2-DIOXARSEPINES

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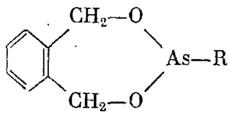
UDC 541.63:541.67:543.422.25:547.879

The conformations of seven-membered heterocycles have been investigated, containing a planar fragment in the ring, heteroatoms in positions 1,3, and the following groupings in position 2: P—R [1-3], S=O [4-5], R$^1$—C—R$^2$ [6], where R, R$^1$, and R$^2$ are organic radicals. In the case of the canonic conformations realized in such molecules (chair, twist) the energy difference is small and the transition barrier is 30-35 kJ/mole or less. The data available on the structure and conformation properties of such heterocycles with a tervalent As atom in position 2 consist only of our short communication [7].

In the present work we have applied $^1H$ and $^{13}C$ NMR, dipole moments (DM) and Kerr constants (KC) to investigate the following compounds



R = Cl (I), Br (II), Ph (III), $C_6H_4Br$-*p* (IV), $C_6H_4NO_2$-*p* (V).

Dipole Moments and Kerr Constants. The DM of compounds (I)-(V) and the KC of compounds (I), (II) have been determined. The geometrical parameters of the seven-membered rings were taken to be the same as those for the six-membered rings with the difference that the angle of COAs was taken to be 120° in all compounds, as in the case of phthalyl esters of phosphoric acids [8]. The geometry of the o-xylylene fragment is the usual [9]. DM and KC were calculated for the three possible conformations (chair-*a* (*a*-C), twist (T), and chair-e (e-C)) by using the parameters of polarity and polarizability of the As bonds [10-12] (from the corresponding six-membered rings) and of the o-xylylene fragment [13]. The experimental and calculated DM and KC are given in Table 1. An analysis of these data shows that the chair form with an equatorial substituent for (I) and (II) can be excluded with confidence (the difference between the constants calculated for *a*-C and e-C is much larger than the deviation from additivity); the DM and KC data do not exclude the presence of a mixture of two other forms. In the case of (III) and (IV) the graphical analysis of DM by Exner's method leads to the conclusion that a mixture of not more than two forms can be present in these compounds: T and *a*-C. Thus, it has been demonstrated by means of electrooptical methods which forms can be present in the conformation mixture. The preferred conformations have been selected by dynamic NMR.

NMR Data. Since no SSV stereospecific constants are available for the compounds investigated, the main NMR test is the nonequivalence of the axial and equatorial protons in the 4,7 positions $\Delta\delta_{ae} = \delta_a - \delta_e$. Changes of the geminal constants $^2J_{H_aH_e}$ are negligible over a wide temperature range (0.5-1 Hz) and can be used therefore only in comparative analysis.

Two groups of compounds can be separated with respect to the changes in the NMR spectra of compounds (I)-(V) with temperature. In one group the NMR spectra of compounds (I) and (II) show no exchange broadening; the observed value of $\Delta\delta_{ae}$ varies only by 0.03-0.05 ppm (increasing with decreasing temperature). The value of $\Delta\delta_{ae}$ changes somewhat when the solvent is changed, however its tendency of changing with temperature remains. For instance, in the case of (I) at 233°K $\Delta\delta_{ae}$ = 1.45 ppm in a mixture of $C_2F_4Br_2 + CS_2$ (1:1 by volume) and 1.42 ppm in

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V. I. Ulyanov-Lenin Kazan' State University. A. M. Butlerov Institute of Chemistry, Kazan' State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimiya, No. 8, pp. 1779-1784, August, 1984. Original article submitted May 10, 1983.

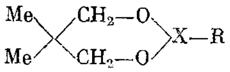
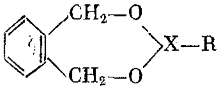
0568-5230/84/3308-1627$08.50

TABLE 1. Calculated and Experimental Values of DM and KC for Compounds (I)-(V)

| Compound, conformation | $\mu$, D | KK | Compound conformation | $\mu$, D |
|---|---|---|---|---|
| (I), *a*-C | 1,69 | 133 | (IV), *a*-C | 1,43 |
| (I), T | 2,35 | 113 | (IV), T | 0,88 |
| (I), *e*-C | 3,75 | −969 | (IV), *e*-C | 2,45 |
| | (2,34) * | (245) | | (1,31) * |
| (II), *a*-C | 1,68 | 122 | (V), *a*-C | 1,95 |
| (II), T | 2,23 | 191 | (V), T | 3,44 |
| (II), *e*-C | 3,48 | −918 | (V), *e*-C | 4,94 |
| | (2,42) | (287) | | (3,79) |
| (III), *a*-C | 2,75 | | | |
| (III), T | 0,91 | | | |
| (III), *e*-C | 0,98 | | | |
| | (1,67) | | | |

*Experimental data in brackets.

TABLE 2. Parameters of the Spectra of Methylene Protons in Chair-*a* Conformation of 5,5-Dimethyl-2-Substituted 1,3,2-Heterocycles (at $C^{4,6}$) and of Their Seven-Membered Heteroanalogs (at $C^{4,7}$)

| Compound | | Solvent | $T$, K | $\delta_H$, ppm | | $\Delta\delta_{ae}$, ppm | $-{}^2J_{ae}$, Hz | Literature reference |
|---|---|---|---|---|---|---|---|---|
| | | | | $\delta_a$ | $\delta_e$ | | | |
|  | | | | | | | | |
| X–R | S=O | $CCl_4$ | 303 | 4,43 | 3,29 | 1,14 | 10,5 | [15] |
| | Sb–OBu-*t* | $CHCl_3$ | 303 | 4,33 | 3,32 | 1,01 | 10,5 | [16] |
| | As–Cl | $CCl_4$ | 303 | 4,28 | 3,56 | 0,72 | 12,0 | [17] |
| | As–Br | $CCl_4$ | 303 | not quoted | | 0,69 | 12,0 | [11] |
| | As–OPh | $CCl_4$ | 303 | 4,34 | 3,37 | 0,97 | 12,0 | [17] |
|  | | | | | | | | |
| X–R | S=O | $C_2F_4Br_2$+ acetone | 173 | 6,36 | 4,50 | 1,86 | 13,5 | [5] |
| | Sb–OBu-*t* | $CHCl_3$ | 223 | 6,03 | 4,64 | 1,40 | 12,5 | [16] |
| (I) | As–Cl | $C_2F_4Br_2$+ acetone | 273 | 6,11 | 4,66 | 1,45 | 13,0 | Present work |
| (II) | As–Br | $C_6H_6+CCl_4$ | 303 | 6,08 | 4,74 | 1,34 | 13,0 | |

$CHCl_3$. Such negligible changes in $\Delta\delta_{ae}$ (2-3% on $\Delta\delta_{ae}$) indicate that in the case of (I) and (II) the conformational equilibrium is shifted towards one of the forms.

The dominating conformation is easily selected and the signals in the spectrum assigned by comparing the NMR spectra of (I) and (II) to those of the corresponding six-membered 1,3,2-heteroanalogs (Table 2). The correctness of this approach is convincingly illustrated on the example of phthalyl sulfite [4, 5].

Numerous experimental data (see references in the literature cited above and in [14, 15]) indicate the axial orientation of the electronegative substituent in the second position in the chair conformation of six-membered 1,3,2-heterocycles. In this conformation (*a*-C) the protons of the 4,6-methylene groups show a strong nonequivalence, whereby the signals of the axial protons lie in a weaker field than the equatorial protons, i.e., a so-called inversion of the chemical shift has occurred (CS).

In the transition to the seven-membered heteroanalogs with a benzofragment these conformational and spectral characteristics are retained; a large value of $\Delta\delta_{ae}$ and a general shift of $H_a$ and $H_e$ signals to the weak field is observed which reflects the specific influence of the aromatic ring on the screening constant of these protons. The absolute value of the geminal constant ${}^2J_{H_aH_e}$ also increases somewhat, depending on the kind of heteroatom in the second position. It can be seen (see Table 2) that these characteristics of the NMR spectrum are

TABLE 3. $^{13}$C NMR Chemical Shifts of (I)-(III) (in ppm; Internal Standard: TMS)

| Compound | Solvent | T, K | δ (±0,2 ppm) | | | |
|---|---|---|---|---|---|---|
| | | | $C^{4,7}$ | $C^{5,6}$ | $C^{8-11}$ | $C^{i}$ |
| (I), *a*-C | $CH_2Cl_2+CCl_4$ | 303 | 68,9 | 139,8 | 129,9, 128,5 | |
| (II), *a*-C | $CDCl_3+CCl_4$ | 303 | 70,9 | 139,5 | 129,9, 128,5 | |
| (III), ⟨*a*-C-T⟩ | $CD_2Cl_2+C_2F_4Br_2$ | 273 | 70,25 | 139,9 | 130,9, 128,8 | 145,7 |
| (III), *a* C | $CD_2Cl_2+C_2F_4Br_2$ | 143 | 70,65 | 140,1 | Not resolved | **Collapse** |
| (III), ⟨T⟩ | | | 69,11 | 138,7 | | |

fully inherent to (I) and (II). The T-form can be eliminated as the dominating conformation since it is characterized by a lower average nonequivalence $\Delta\delta_{ae}$ as well as by a significantly higher absolute average geminal constant $^2J_{H_aH_e}$ (for instance, in the case of phthalyl sulfite [5] $\langle\Delta\delta_{ae}\rangle \simeq 0.3$ ppm, $\langle^2J_{H_aH_e}\rangle \approx 15$ Hz.

The $^{13}$C NMR spectra of (I) and (II) (Table 3) are also not subject to changes over a wide range of temperatures; the chemical shifts $\delta^{13}$C of the $C^{4,7}$ carbon atoms correlate satisfactorily with the $\delta^{13}$C values of $C^{4,6}$ atoms in the *a*-C conformation for the corresponding six-membered heteroanalogs [14]. Thus, the NMR data show unequivocally the domination of a *a*-C conformation of compounds (I) and (II).

Compounds (III)-(V) are characterized by a very small $\Delta\delta_{ae}$ value which complicates the assignment of the proton signals of the methylene fragment. In the case of (III) and (IV) the shifts at ∿20° in a mixture of solvents $C_2F_4Br_2$ + $CS_2$ (1:1 by volume) are equal to 5.16, 5.06 and 5.10, 5.00 ppm, respectively; in the case of (V) (in $CS_2$) these lines are not resolved ($\delta_{H_a} \sim \delta_{H_e} \approx 5.11$ ppm). The NMR spectra show signs of exchange broadening at T ∿ 120°K, however, a clear separation of the lines was not achieved due to the low value of $\Delta\delta_{ae}$ which changes negligibly in the case of (III) (∿0.01 ppm); in the case of (IV) and (V) it increases to 0.07 and 0.17 ppm, respectively, when cooled to 200°K.

Such a negligible nonequivalence of the chemical shift is somewhat unexpected if we take into account that it is much larger in the 2*a*-C conformation of 2-phenyl-1,3,2-dioxarsenane, of the order of 0.18 ppm (assessed on the basis of data given in [11]); a tendency towards a significant increase in $\Delta\delta_{ae}$ is observed in the transition to the seven-membered heteroanalogs with the benzofragment in the ring. These characteristics of the NMR spectra of (III)-(V) are easily explained if we assume that two conformers are present in the solution in comparable amounts under conditions of rapid exchange on the NMR scale. The value of $\Delta\delta_{ae}$ in alternative conformations have the opposite sign, i.e., in one of them there is no reversal of the chemical shift. Such a situation is encountered, for instance, in the exchange pair *a*-C ↔ T for phthalyl sulfite [5]. The determination of the dominating conformation based solely on $\Delta\delta_{ae}$ values is extremely laborious.

In the case of (III)-(V) at ∿20° the geminal constant is larger than the values of the constant that characterize the conformation *a*-C of (I) and (II) (13.0 Hz, see Table 2). This points unambiguously to the participation of the twist form in the equilibrium and at the same time eliminates the e-C conformation, for which the geminal constant in 6-membered 1,3-heterocycles must be the same as in the *a*-C conformation while a reversal of the chemical shift is not observed.

In the temperature range 173-353°K the geminal constant $^2J_{H_aH_e}$ for (III) and (V) remains the same, equal to 13.9 Hz. By taking into account the invariability of the value of $\Delta\delta_{ae}$ in (III) and its negligible increase in (V) in the same temperature interval, we can assume that the conformational free energy of the equilibrium *a*-C—T—$\Delta G_{C-T}$ for (III) and (V) is close to 0. A negligible decrease in $^2J_{H_aH_e}$ (absolute value) is observed in the case of (IV) from 14.2 to 13.7 Hz which indicates a small domination of the *a*-C conformation.

The $^{13}$C NMR spectra of (III) at 22.4 MHz show an exchange broadening at 150°K; however, a separation of the lines was not achieved down to ∿120°K. The rotation of the phenyl substituent around the As—C bond at these temperatures cannot be suppressed [18]; consequently, this exchange broadening must be related to a retardation of the C—T conversion. Splitting of the signals of carbons $C^{5,6}$ and $C^{4,7}$ was achieved at the frequency of 62.9 MHz at T = 143°K.

TABLE 4. Coefficients of Equations Used for the Calculations, Dipole Moments, Kerr Constants of Compounds (I)-(V)

| Compound | $\frac{\Delta\varepsilon}{\Delta\omega_2}$ | $\frac{\Delta n_D}{\Delta\omega_2}$ | $\frac{\Delta n_D^2}{\Delta\omega_2}$ | $\beta$ | $\delta$ | $\mu$, D | $_mK \cdot 10^{12}$ |
|---|---|---|---|---|---|---|---|
| (I) | 4,705 | 0,139 | 0,406 | 0,246 | 134,240 | 2,34 | 245 |
| (II) | 4,440 | 0,161 | 0,471 | 0,229 | 132,773 | 2,42 | 287 |
| (III) | 2,569 | – | 0,666 | – | – | 1,67 | – |
| (IV) | 1,757 | – | 0,814 | – | – | 1,31 | – |
| (V) | 5,860 | – | 0,454 | – | – | 3,79 | – |

The signal $C^1$ of the aromatic ring, connected to the As atom collapses at this temperature while the other signals of both aromatic fragments are strongly broadened and are not resolved.

The resolved lines of the $^{13}C$ NMR spectra of frozen conformers of (III) were assigned on the basis of the analysis of the chemical shift of the $C^{5,6}$ atoms of the corresponding conformers of (I)-(III), phthalyl sulfite (VI) [5], phthalyl formal (VII), and its 2-phenyl derivative (VIII) [19]. Thus, in the *a*-C conformation these shifts are equal to 139.8 (I), 139.5 (II), 138.2 (VI), 139.9 (VII), 139.8 (VIII), and in the averaged twist conformation 135.1 (VI), 138.7 (VII), and 138.4 ppm (VIII). It can be seen that the values of $\delta^{13}C$ ($C^{5,6}$) in the phthalyl esters are practically independent on the type of substituent in the position 2; the difference between the two conformations ($\Delta\delta^{13}C = \delta^{13}C(C) - \delta^{13}C(T)$) depends mainly on the difference in the mutual orientation of $C^{5,6}$—$C^{4,7}$ and $C^{4,7}$—O bonds in these conformations. Thus, the high-intensity line at $\delta^{13}C$ 138.7 ppm must be assigned to the twist conformation (averaged), while the line at $\delta^{13}C$ 140.1 ppm belongs to the *a*-C conformation. The assignments of the $C^{4,7}$ lines have been made in Table 2.

The ratio of the intensities of the separated $C^{5,6}$ signals is equal to 3:2; this corresponds to the assumption that the free energies of the two conformers are similar, with account of a double degeneration of the twist form ($-\Delta G_{C-T}$ = 500 ± 100 J/mole in favor of the chair form at T 143°K). The free activation energy of the C—T conversion at $T_c$ 153°K is equal to 26.0 ± 2 kJ/mole and is typical for this series of heterocycles.

The compounds of tervalent As are characterized by a high configurational stability; experimental and theoretical assessments give values of more than 100 kJ/mole for the inversion barriers of As(III). Configuration reversals have been observed only at certain conditions in the presence of arsenic chlorides or other chlorine compounds, due to chlorine exchange in associates of the type substance—solvent, for instance in 2-chloro(bromo)-1,3,2-dioxarsolanes and 2-chloro(bromo)-1,3,2-arsenanes [17, 14], and in autoassociates in the series of cyclic acid chlorides of arsenous acid by mass spectrometry [20].

The configurational stability of As(III) is also apparent in the investigated compounds (I)-(V); it is evidently characteristic for all cyclic compounds of this type. Configuration reversals were observed in (I) and (II) already at ∿20° when 2-3% $AsCl_3$ was added.

## EXPERIMENTAL

DM and KC were measured at 25° in $CCl_4$ (I)-(IV) and dioxane (V); the results are given in Table 4.

The $^1H$ NMR spectra were recorded on a Varian HA-100D spectrometer, the $^{13}C$ NMR spectra on Bruker-Physik W-90 and WM-250 spectrometers. The precision of measuring the specimen temperature was ±2°K; the sensor was thermostated by means of commercial temperature control attachments.

2-Chloro-5,6-benzo-1,3,2-dioxarsepin (I). A mixture of 5.65 g phthalyl alcohol [21] and 5.73 g triethyl arsenite was heated for 30 min and the ethanol distilled off. The residue was kept in vacuum for 5 h at 120-130°K (9 mm); 2.5 g $AsCl_3$ was added and the mixture heated for 4 h at 130-140°K (9 mm) and purified by sublimation at 110-115°K (9 mm); mp 90-92°K, yield 90%. Found: C 38.67; H 3.39; As 30.09; Cl 14.81%. $C_8H_8O_2AsCl$. Calculated: C 38.97; H 3.27; As 30.39; Cl 14.38%.

2-Bromo-5,6-benzo-1,3,2-dioxarsepin (II). A mixture of phthalyl alcohol (5 g) and 5.2 g triethyl arsenite was heated for 30 min and the ethanol distilled off. After keeping the residue in vacuum for 5 h, 3.8 g $AsBr_3$ was added and the mixture heated for 4 h at 120-130°K

(9 mm). The product was purified by sublimation at 120-125°K (9 mm), yield 90%, mp 116°K. Found: C 32,80; H 2.97; As 25.27; Br 27.59%. $C_8H_8O_2AsBr$. Calculated: C 33.01; H 2.79; As 25.75; Br 27.47%.

2-Phenyl-5,6-benzo-1,3,2-dioxarsepin (III). 5 g o-phthalyl alcohol and 7.75 g of the dimethyl ester of phenylarsonous acid was heated for 30 min in an Arbuzov flask; the methanol was then distilled off. The rest was kept in vacuum for 7 h at 150-170°K (8 mm) and the product purified by sublimation at 175-185°K (10 mm). Colorless crystals were obtained which hydrolyzed rapidly in air, mp 84-86°K, yield 90%. Found: C 57.86; H 4.24; As 25.58%. $C_{14}H_{13}O_2As$. Calculated: C 58.34; H 4.54; As 25.99%.

2-(p-Bromophenyl)-5,6-benzo-1,3,2-dioxarsepin (IV). Product prepared like (III) from 2.63 g o-phthalyl alcohol and 5.6 g dimethyl ester of p-bromophenyl-arsenous acid. The product was purified by reprecipitation from cyclohexane and petroleum ether (40-60°K), mp 88-90°K, yield 90%. Found: C 45.47; H 3.36; As 20.19; Br 21.61%. $C_{14}H_{12}O_2AsBr$. Calculated: C 45.81; H 3.30; As 20.41; Br 21.76%.

2-(p-Nitrophenyl)-5,6-benzo-1,3,2-dioxarsepin (V). Product prepared like (III) from 2.9 g o-phthalyl alcohol and 5.4 g dimethyl ester of p-nitrophenylarsonous acid. The residue was kept in vacuum for 4 h at 125-135°K (10 mm) and the product purified by recrystallization from benzene, mp 159°K, yield 90%. Found: C 50.96; H 3.78; As 22.22; N 3.83%. $C_{14}H_{12}O_4AsN$. Calculated: C 50.47; H 3.63; As 22.49; N 4.20%.

The authors wish to express their gratitude to I. É. Ismaev for the recording of the $^{13}C$ NMR spectra and to A. V. Il'yasov and A. N. Vereshchagin for the discussion of the results.

## CONCLUSIONS

1. 2-Chloro- and 2-bromo-5,6-benzo-1,3,2-dioxarsepines have the chair conformation with axial arrangement of the exocyclic bond at the arsenic atom.

2. In the case of 2-phenyl-, 2-(p-bromophenyl)-, and 2-(p-nitrophenyl)-5,6-benzo-1,3,2-dioxarsepines an equilibrium exists in solution between the chair-*a* and twist conformers, the ratio of which is close to unity. $^{13}C$ NMR spectra of "frozen conformers" at 143°K have been obtained for the first time for such a series of compounds.

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# COMPLEXES OF PYROMELLITIC DIANIL ACID WITH APROTIC SOLVENTS

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UDC 541.49:547.585:547.551:542.61

Complexing with the participation of polar aprotic solvents plays an important role in all stages of the synthesis of imides and polyimides. The starting compounds, especially dianhydrides, thus form sufficiently stable complexes with dimethylformamide (DMFA) and other solvents of the amide type [1, 2]. The reactivity of these complexes in acylation of aromatic amines is lower than the starting dianhydrides [3]. It was interesting to study the role of complexing in the subsequent stages of the reaction: in the formation and cyclodehydration of the amido acid.

Crystalline complexes of A with DMFA (dimethylformamide) (I), DMAA (dimethylacetamide) (II), MP (N-methyl-2-pyrrolidone) (III), and DMSO (dimethyl sulfoxide) (IV) which are stable in prolonged storage in air were first isolated as a result of precipitation with acetone or benzene from solutions of pyromellitic dianil acid (A) in DMFA, DMAA, MP, and DMSO. Acid A free of solvent was synthesized for comparison and control. The compounds isolated were colorless crystalline powders. Significant differences were observed in the IR spectra* of acid A and product (I) (Fig. 1). In the 20-110°C range where the reaction of cyclization of the amido acid group is excluded, frequency shifts of two absorption bands were observed in the spectrum of (I): 1685 $cm^{-1}$, assigned to bound DMFA, and 1545 $cm^{-1}$ (amide II), assigned to the amido acid component of the complex. The values of the shifts were equal to 10 $cm^{-1}$ (DMFA, maximum high-frequency shift) and 5 $cm^{-1}$ (amide II, low-frequency shift), and these changes in the spectrum were reversible with respect to the temperature. This indicates the appearance of hydrogen bonds in these compounds, which is evidence of A—DMFA complexing in product (I), probably based on the donor—acceptor reaction of acid A and the organic base (DMFA). The findings of the elemental analysis (Table 1) of compounds (I)-(IV) differ from the calculated data for pure acid A, but are in good agreement with the calculated data for the compounds in which two molecules of the corresponding solvent are required per molecule.

Compounds (I)-(IV) were studied by mass spectrometric thermal (MTA) and thermogravimetric (TGA) analysis (Figs. 2-5).

Three peaks can be distinguished on the (MTA) curves of compounds (I)-(IV) (see Figs. 2a-5a) and correspond to elimination of the solvent, water, and aniline. When the sample was gradually heated (at the rate of 2°/min), the complex decomposed with liberation of the corresponding solvent and subsequent cyclodehydration and partial decomposition of acid A with liberation of aniline. For performing quantitative calculations, the mass spectrometer was calibrated with binary mixtures of water and the solvents used and with a mixture of water and aniline. The results of the calculations (see Table 1) showed that compounds (I)-(IV) had the composition of $[A]_1 \cdot [Sol]_2$, where Sol is a molecule of solvent, regardless of the type of solvent. The presence of complexing with the solvent and the type of solvent significantly affected the process of thermal transformations of A. Although the decomposition of the amido acid of compounds (I) and (II) was almost the same and relatively low (3 and 2%, respectively), it attained 6% for compound (III), 11% for (IV), and 13% of pure amido acid A was decomposed in the same conditions.

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*The IR spectra were made by A. N. Krasovskii.

Institute of High-Molecular Compounds, Academy of Sciences of the USSR, Leningrad. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1784-1788, August, 1984. Original article submitted May 16, 1983.

0568-5230/84/3308-1632$08.50