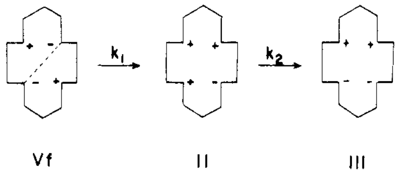

Figure 4. Proposed configurational isomers involved in the isomerization of *cis*-Ni([14]aneN_4)$(H_2O)_2^{2+}$.

3 shows the variation of effective molar absorptivity as a function of perchloric acid concentration. The molar absorptivity of the complex is 100 M^{-1} cm^{-1}, in contrast to that of "normal" Ni([14]aneN_4)$^{2+}$, which has a molar absorptivity of 64. From relatively concentrated solutions of perchloric acid, crystals of α-Ni([14]aneN_4)$(ClO_4)_2$ can be isolated. The perchlorate concentrations necessary to stabilize the α planar form are quite high and are similar to those necessary to produce the low-spin form of Ni(trien)$^{2+}$.[9,10]

The isomeric complex, α-Ni([14]aneN_4)$^{2+}$, must be a configurational isomer, in which the nitrogens have a different configuration than that of the stable β isomer. (The unstable isomer is designated the α isomer in conformity with the designations applied to similar configurational isomers of (*rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(2+) by Curtis[11].) The stable planar Ni([14]aneN_4)$(ClO_4)_2$ has structure III,[12] in which the five-membered rings are gauche and the six-membered rings adopt the chair form. This geometry, the lowest energy of the five possible planar forms,[13] has two amine hydrogens on adjacent nitrogens above the plane of the complex, while the other two are below the plane.

The α planar complex presumably has the same nitrogen configuration as the folded isomer Vf.[13] Two amine hydrogens on opposite nitrogens are above the plane (structure II). No kinetic evidence was found to suggest otherwise: dissolution of orange α-Ni([14]aneN_4)$(ClO_4)_2$ in water gave violet solutions of *cis*-Ni([14]aneN_4)$(H_2O)_2^{2+}$, and these solutions isomerized to the stable planar form at the same rate as solutions prepared from the original samples of the folded isomer.

A reasonable kinetic scheme for isomerization would require the successive inversion of two amine protons (Vf → II → III). The isomerization reaction was found to be acid and base catalyzed, first order in either $[H^+]$ or $[OH^-]$.[1] Since two protons are being inverted, yet the reaction is only first order in acid or base, it is necessary to postulate that the second inversion is more rapid than the first. Base catalysis likely arises from the familiar conjugate-base mechanism. Ionization of an amine proton on the nitrogen to be inverted could provide a simple pathway for inversion. Acid catalysis may occur via the mechanism recently suggested by Margerum.[8,14] At relatively high proton concentrations, a metal–nitrogen bond may be broken and the nitrogen protonated before the metal ion is solvated. This may require a relatively modest lengthening of the metal–nitrogen bond distance before the metal–nitrogen bond is effectively "broken". This mechanism, which gives rise to a $[H^+]$ dependence of dissociation rates, is particularly applicable to dissociation reactions of macrocycles, where the donor atoms are constrained by the ligand structure to remain close to the metal ion.

In summary, generation of the folded isomer of Ni([14]aneN_4)$^{2+}$ permits the examination of isomerization and dissociation pathways in acid solution and has provided an estimate of the extremely slow rate of acid dissociation of Ni([14]aneN_4)$^{2+}$. Because of the extreme kinetic inertness of the [14]aneN_4 complex, a systematic study of the acid dissociation rate law is difficult. The [13]aneN_4 complex, a more labile system, will permit a fuller elucidation of the mechanism of dissociation of a nickel(II)–N_4 macrocyclic complex.[15]

Registry No. *cis*-Ni([14]aneN_4)$(H_2O)_2^{2+}$, 78684-35-2; Ni([14]aneN_4)$^{2+}$, 46365-93-9.

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Contribution from the Department of Chemistry,
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1,2-Bis(*F*-alkyl)cyclo-1,2-diaza-3-sulfanes, 1,2-Bis(*F*-alkyl)cyclo-1,2-diaza-3,4,5-trisulfanes, and 1,2-Bis(*F*-alkyl)cyclo-1,2-diaza-3,4,5,6-tetrasulfanes, $\overline{R_fN\text{-}S_x\text{-}NR_f}$ (x = 1, 3, 4)

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Received May 5, 1983

A new class of sulfur–nitrogen heterocyclic compounds with the general formula $\overline{R_fN\text{-}S_x\text{-}NR_f}$ (where $R_f = CF_2Cl$ or C_2F_5 and x = 1, 3, or 4) results from the photolysis of $R_fN{=}NR_f$ and S_2Cl_2. These heterocyclic compounds are pale yellow, high-boiling liquids that decompose on standing at 25 °C. The new compound $CF_2ClN{=}NCF_2Cl$ was synthesized by photolysis of CF_2ClNCl_2 at 0 °C.

Introduction

In the chemistry of inorganic heterocycles, sulfur–nitrogen compounds are important both historically and currently. Tetrasulfur tetranitride, first prepared in 1835, is one of the oldest and most studied of all inorganic heterocycles, yet its chemistry still challenges the imagination. There are a very large number of cyclic sulfur–nitrogen compounds in which the nitrogen atoms are in the 1,3- or 1,4-positions, e.g., N_2S_2, $N_2S_3^+$, N_2S_4, $N_3S_4^+$, and N_4S_4, but there are few examples of cyclic sulfur–nitrogen heterocyclic compounds in which the nitrogen atoms are vicinal.[2,3] While the synthesis of these

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(1) Present address: Department of Chemistry, Baldwin-Wallace College, Berea, OH 44017.
(2) Roesky, H. W. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 240 and references therein.

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1,2-diaza derivatives has not resulted from the interaction of hydrazine itself with chlorosulfanes, the oxidatively stable hydrazinedicarboxylate, $(RO_2CNH-)_2$, has been condensed with S_xCl_2 (x = 1,2,6) to form $\overline{\mathrm{YNN(Y)SSN(Y)N(Y)SS}}$, $\overline{\mathrm{YNSSSSSSNY}}$, and $\overline{\mathrm{YNN(Y)SN(Y)N(Y)S}}$ (where Y = RO_2C).[4,5] However, none of the Y groups contains fluorine.

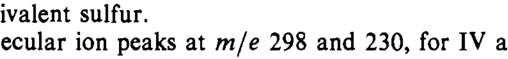
Here we report the syntheses and physical properties of three-, five-, and six-membered sulfur-nitrogen ring compounds that formally contain sulfur(II) and that have the nitrogen atoms occupying the 1,2-positions. These new heterocycles were prepared by photolyzing *N,N'*-bis(*F*-alkyl)diazenes, $R_fN{=}NR_f$ (R_f = CF_2Cl or C_2F_5), with S_2Cl_2 at 0 °C.

Results and Discussion

It has been suggested that the only three-membered rings, other than thiirane derivatives, to be more stable than their ring-opened isomers are the 1,1-dioxides of thiaziridines and of thiadiazirdines.[6] Such a three-membered ring composed of heteroatoms has been verified by X-ray analysis: $\overline{\mathrm{RNSO_2NR}}$, where R is $(CH_3)_3CCH_2C(CH_3)_2$–, which helps to stabilize the ring. The tetracoordinate sulfur is formally S(VI).[7-9] Dinitrogen can be added to the benzenesulfenium cation to form a cyclic adduct, but whether the nitrogen forms a side-on or end-on product was not demonstrated with certainty.[10]

However, there is no report of three-membered rings with divalent sulfur and two nitrogen atoms. The instability of such three-membered rings is attributed to repulsion between the electron lone pairs on sulfur and on the nitrogen atoms.[2] The interactions of these lone pairs should be diminished if strong electron-withdrawing groups are attached to the nitrogen atoms. Thus, it has been possible to prepare this new compound type in modest yields with CF_2Cl or C_2F_5 as the electronegative substituent on the nitrogen atoms via the reactions

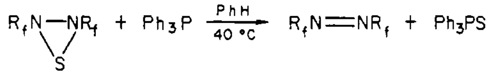
$$R_fNCl_2 \xrightarrow[\text{quartz}]{\text{UV}} R_fN{=}NR_f + Cl_2{}^{11,12}$$



IV, $R_f = C_2F_5$[13]
V, $R_f = CF_2Cl$

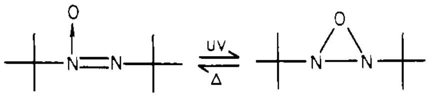
When equimolar amounts of $R_fN{=}NR_f$ and S_2Cl_2 were photolyzed in a quartz vessel, the three-membered slightly volatile heterocycles were isolated in about 5% yield. These compounds are high-boiling yellow liquids with vapor pressures of 9 and 11 torr at 25 °C for IV and V, respectively. We believe that IV and V are the first examples of such compounds with divalent sulfur.

Molecular ion peaks at *m/e* 298 and 230, for IV and V, respectively, are observed. The next highest mass numbers are at *m/e* 266 (IV) and 163 (V), which are assigned to $C_2F_5NNC_2F_5$ [$(M-S)^+$] and $CF_2ClNNCF_2$ [$(M-S-Cl)^+$] and which led us to suggest a cyclic structure. Molecular weight measurements give 291 for IV (theoretical 298). Compound IV was purified via gas chromatography, which precludes the presence of $CF_3CF_2N{=}NCF_2CF_3$ as an impurity, although complete separation from S_2Cl_2 was not achieved. When either compound was reacted with triphenylphosphine at 40 °C in benzene as solvent, desulfurization occurred and $(R_fN{=})_2$ was obtained in quantitative yield, which supports a cyclic rather than an acyclic diimide geometry.[4]



Of alternate structures, the most plausible is the acyclic $CF_3CF_2N{=}S{=}NCF_2CF_3$ (VI).[14] However, a comparison of spectral data demonstrates conclusively that IV is different. ^{19}F NMR: for IV, ϕ −83.3 (CF_3), −112.5 (CF_2); for VI, ϕ −88.8 (CF_3), −94.4 (CF_2). In a hydrazine derivative such as $CF_3CF_2N(NF_2)N(F)CF_2CF_3$, where the nitrogen that is bonded to $>CF_2$ is three coordinate, the ^{19}F NMR shift for CF_2 is ϕ −110.7, which is very close to that in the parent $CF_3CF_2N{=}NCF_2CF_3$ and in our cyclic product. Moreover, comparing chemical shifts for the CF_2 group in sulfimide molecules such as $CF_3CF_2N{=}SX_2$, $CF_3CF_2N{=}S{=}NCH_3$, $CF_3CF_2N{=}S(O)F_2$, and $CF_3CF_2N{=}S(F_2){=}NCF_2CF_3$ shows that the range is ϕ −70 to −97. Thus, the methylene group in IV exists in an environment that does not involve a sulfimide link but rather one similar to that of the starting diazene.

Since the oxygen analogue (R = *tert*-butyl) of our three-membered rings is known[15,16] and since these oxadiaziridines are somewhat labile reverting to their valence isomers, azoxyalkanes, at 25 °C in a few hours



it is appropriate to consider a similar mode of behavior for $(C_2F_5N)_2S$. The presence of a thioazoxy isomer, $CF_3CF_2N^+(S^-){=}NCF_2CF_3$, or a rapid equilibrium between the latter and the cyclic structure is unlikely on the basis of infrared data. The highest bands observed at 1245 and 1180 cm^{-1} are assigned to ν_{C-F}, causing the assignment of ν_{N-N} to a lower energy band. In fluorinated azoxy compounds, $\nu_{N=N}$ occurs about 100 cm^{-1} higher than in the corresponding diazenes [$(-N^+(O^-){=}N-$ vs. $-N{=}N-$, 1525 vs. 1425 cm^{-1}]. In the infrared spectrum of $CF_3CF_2\overline{\mathrm{NSN}}C_2F_5$ there are no bands higher than those in the parent diazene, where the highest band is at 1346 cm^{-1}.[12] In the thioazoxy isomer, the CF_2 groups would be chemically nonequivalent, as is observed in nonfluorinated systems,[15] but only a single resonance is observed in the ^{19}F NMR spectrum.

An even less likely structure that might be proposed is $(R_f)_2N{-}N{=}S$. This species would likely react with Ph_3P, giving Ph_3PS, but it would be highly unlikely for the other product to be $(R_fN)_2$, which is obtained in essentially quantitative yield. If nitrogen were lost (there is none formed), the other product would be the hydrazine $(R_f)_2NN(R_f)_2$ or perhaps C_4F_{10}. Since nitrogen is not lost, the tetrazene $(R_f)_2NN{=}NN(R_f)_2$ could be the product, but it is not observed. Additionally, $\nu_{N=S}$ in the infrared spectrum would be expected to be higher than the highest band that is observed for, e.g., IV, which is 1245 cm^{-1}. There seems to be no support for this isomer. Thus, it can be concluded that the $R_f\overline{\mathrm{NSN}}R_f$ is indeed cyclic.

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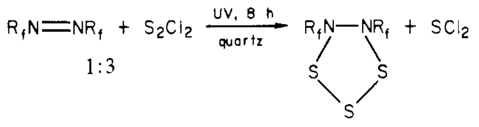
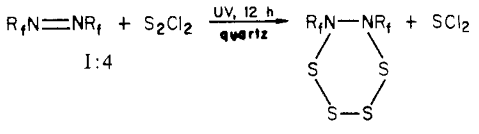
When the stoichiometry of the reaction is changed, five- and six-membered heterocycles with vicinal nitrogen atoms are obtained in low yield.



7–9%

VII, $R_f = CF_3CF_2$
VIII, $R_f = CF_2Cl$

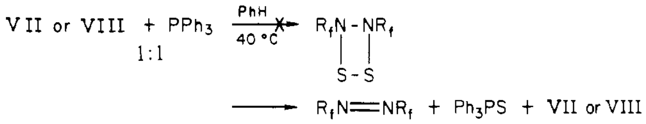


9–11%

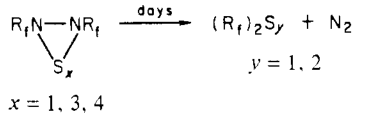
IX, $R_f = CF_3CF_2$
X, $R_f = CF_2Cl$

While many N_2S_3 and N_2S_4 compounds have been synthesized, it is believed that these are the first examples that contain vicinal nitrogen atoms and *F*-alkyl substituents on nitrogen. Compounds VII–X are high-boiling yellow liquids with vapor pressures of 4, 7, 6, and 8 torr, respectively, at 25 °C. As was the case for IV, a molecular ion is observed in the mass spectrum for IX. For VII, VIII, and X, the highest *m/e* values found are $M^+ - 2F$, $M^+ - Cl$, and $M^+ - Cl$, respectively. However, in each case, a stepwise elimination of sulfur atoms occurs. The same argument as was made for IV, involving ^{19}F NMR shifts of the fluorine atoms in the CF_2 groups of CF_3CF_2 to support cyclic rather than acyclic species, can be employed here. Both MS and NMR support strongly the proposed cyclic structures.

Additionally, the reaction of triphenylphosphine with VII–X gives quantitative yields of Ph_3PS and $R_fN{=}NR_f$. When it was impossible to form R_fNSSNR_f by the reaction of $R_fN{=}NR_f$ with S_2Cl_2 in a 1:2 molar ratio, both VII and VIII were reacted with triphenylphosphine in a 1:1 molar ratio in an effort to remove only a single sulfur. The parent diazene was obtained, leaving appropriate amounts of the heterocycle unreacted.



All of the new heterocycles decompose on long standing at 25 °C in Pyrex glass to bis(*F*-alkyl)sulfane and -disulfane and nitrogen.



These are rather surprising products but less so when one considers that when $CF_3N{=}NCF_3$ is passed through a zone of refluxing sulfur at atmospheric pressure during a 3-h period, the product isolated is the acyclic $(CF_3)_2S_3$ and nitrogen.[17]

Although *m*-chloroperbenzoic acid does form a disulfoxide with YNN(Y)SN(Y)N(Y)S (where Y = RO_2C),[18] it does not oxygenate or react with IV or V to form the >S(O) or >SO_2 analogues. This can be attributed to the lower availability of the electron pairs on sulfur in the *F*-alkyl nitrogen compounds.

Thus, by the photolysis of bis(*F*-alkyl)diazenes with disulfur dichloride, it has been possible to prepare a new family of heterocycles, $R_fN{-}S_x{-}NR_f$, in which the nitrogen atoms are vicinal and have *F*-alkyl substituents. This series of compounds results from one of the rather rare reactions where addition is successfully carried out at a nitrogen–nitrogen double bond.

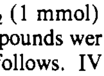
Experimental Section

Materials. $CF_3CF_2NCl_2$,[12] $(CF_3CF_2N{=})_2$,[12] and CF_2ClNCl_2[11] were prepared according to the literature methods. Chlorine fluoride (Ozark-Mahoning), cyanogen chloride (K & K Laboratories, Inc.), disulfur dichloride (Eastman Kodak), and trifluoroacetonitrile (PCR) were used as received.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex-glass vacuum system equipped with a Heise Bourdon tube gauge. Most of the starting materials and products were measured quantitatively with the use of *PVT* techniques. Photolysis reactions were carried out in quartz vessels by using a Hanovia utility ultraviolet quartz lamp. Products were purified by fractional condensation (trap-to-trap distillation) and by using a Wilkins Aerograph Model A-90-P gas chromatograph. Infrared spectra were recorded on a Perkin-Elmer 599B spectrometer with a 10-cm cell and KBr windows. ^{19}F NMR spectra were obtained on a JEOL FX-90Q Fourier transform nuclear magnetic resonance spectrometer by using CCl_3F as an internal standard. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E spectrometer operating at an ionization potential of 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany, and by the University of Idaho.

Preparation of 1,1,1′,1′-Tetrafluoro-1,1′-dichloroazomethane, $ClF_2CN{=}NCF_2Cl$. Dichloro(difluorochloromethyl)amine, CF_2ClNCl_2 (5 mmol), was condensed into a quartz reaction vessel at −196 °C. The vessel was warmed to 0 °C, and the compound was photolyzed at this temperature for about 4 h. After trap-to-trap distillation, $(CF_2ClN{=})_2$ stopped in traps at −78 and −95 °C in about 60% yield. Its infrared spectrum has bands at 1160 s, 1100 s, 940, 930 s (doublet), 890 w, and 740 w cm^{-1}. A molecular ion is not observed in the mass spectrum, but peaks at *m/e* 163 ($M^+ - Cl$, $CF_2ClNNCF_2^+$, 5.9), 128 ($CF_2NNCF_2^+$, 5.9), 85 (CF_2Cl^+, 8.8), and 61 ($NCCl^+$, 100) are observed. The ^{19}F NMR spectrum has a singlet at ϕ −57.6. Anal. Calcd for $(CF_2ClN{=})_2$: C, 12.12; N, 14.14. Found: C, 11.83; N, 13.69.

General Preparation. All of the heterocyclic compounds, i.e.



($R_f = C_2F_5$ or CF_2Cl; $x = 1, 3$, or 4), were prepared in essentially the same manner. In a typical reaction, 1 mmol of *N,N′*-bis(*F*-alkyl)diazene, $R_fN{-}NR_f$, was condensed into a 150-mL quartz vessel, and a stoichiometric amount of disulfur dichloride, S_2Cl_2, was added. The mixture was photolyzed for 4–12 h at either 0 or 25 °C. Initial separations were accomplished via fractional condensation and were followed by gas-chromatographic purification.

Preparation of IV and V. $R_fN{=}NR_f$ (where $R_f = CF_3CF_2$ or CF_2Cl) (1 mmol) and S_2Cl_2 (1 mmol) were photolyzed in a quartz vessel for 4 h. Both the compounds were obtained in about 5% yield. The infrared spectra are as follows. IV: 1245 s, 1180 s, 1080 s, 715 vw, 530 cm^{-1}. V: 1290 br, 1130 s, 1110 s, 930 s, 915 s, 800 m cm^{-1}. The molecular weight of $(CF_3CF_2N)_2S$ was found to be 291 (theoretical 298) by *PVT* techniques. A molecular ion is observed in both the compounds at *m/e* 298 ($(CF_3CF_2N)_2S^+$, 2) and 230 ($(CF_2ClN)_2S^+$, 5). The other principal peaks follow. IV: 266 ($CF_3CF_2NNCF_2CF_3^+$, 1), 119 ($CF_3CF_2^+$, 24.5), 69 (CF_3^+, 100), 64 (S_2^+, 4). V: 163 ($CF_2ClNNCF_2^+$, 13), 128 ($CF_2NNCF_2^+$, 8), 85 (CF_2Cl^+, 9), 64 (S_2^+, 3), 61 ($NCCl^+$, 100). The ^{19}F NMR spectrum of IV shows two singlets at ϕ −83.3 (CF_3) and −112.5 (CF_2) in the ratio of 3:2. A singlet at ϕ −61.4 is obtained in he ^{19}F NMR spectrum of V.

Preparation of VII and VIII. $R_fN{=}NR_f$ (where $R_f = CF_3CF_2$ or CF_2Cl) (1 mmol) and S_2Cl_2 (3 mmol) were photolyzed in a quartz vessel for 8 h. Both the compounds were obtained in 7–9% yield. The infrared spectra are as follows. VII: 1290 s, 1235 s, 1155 w, 1130 m, 1030 m, 710 m cm^{-1}. VIII: 1310 s, 1220 m, 1195 m, 1140 m, 1040 br, 590 cm^{-1}. The molecular weight of VII is found to be 363 (theoretical 362). The molecular ion peak was not observed in either

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Inorg. Chem. **1984**, *23*, 241-247

of these compounds. The other principal fragments obtained are the following. VII: 324 ($CF_2CF_2NNCF_2CF_2S_3^+$, 6.1), 260 ($(CF_2CF_2)_2N_2S^+$, 9.2), 229 ($CF_3NNCF_2CF_2S^+$, 30.3), 119 ($CF_3CF_2^+$, 15.1), 69 (CF_3^+, 100), 64 (S_2^+, 2.4). VIII: 259 ($CF_2ClNNCF_2S_3^+$, 3.1), 227 ($CF_2ClNNCF_2S_2^+$, 2.3), 195 ($CF_2ClNNCF_2S^+$, 1.6), 163 ($CF_2ClNNCF_2^+$, 4.6), 128 ($CF_2NNCF_2^+$, 7.4), 85 (CF_2Cl^+, 11), 64 (S_2^+, 0.9), 61 ($NCCl^+$, 100). The ^{19}F NMR spectrum of VII shows two singlets at ϕ −87.3 (CF_3) and −113.0 (CF_2) in the ratio of 3:2. A singlet at ϕ −62.3 is obtained in ^{19}F NMR spectrum of VIII.

Anal. Calcd for $(CF_3CF_2N)_2S_3$: S, 26.52. Found: S, 25.67. Calcd for $(CF_2ClN)_2S_3$: S, 32.65. Found: S, 31.8.

Preparation of IX and X. $R_fN{=}NR_f$ ($R_f = CF_3CF_2$ or CF_2Cl) (1 mmol) and S_2Cl_2 (4 mmol) were photolyzed in a quartz vessel for 12 h. Both the compounds were obtained in 9–11% yield. The infrared spectra are as follows. IX: 1290 s, 1235 s, 1170 br, 1130 m, 1100 w, 1030 m, 715 w cm^{-1}. X: 1280 s, 1220 m, 1180 s, 1140 m, 1050 br, 580 m cm^{-1}. Vapor pressures of IX and X at room temperatures are 4 and 7 torr, respectively. The molecular weight of IX is found to be 390 (thoretical 394). The molecular ion peak was observed in IX at *m/e* 394. The other principal peaks obtained follow. IX: 356 ($(CF_2CF_2N)_2S_4^+$, 3.1), 324 ($(CF_2CF_2)_2N_2S_3^+$, 3.1), 292 ($(CF_2CF_2)_2N_2S_2^+$, 7.8), 260 ($(CF_2CF_2)_2N_2S^+$, 6.25), 229 ($CF_3CF_2NNCF_2S^+$, 68.7), 160 ($CF_2CF_2N_2S^+$, 21.8), 146 ($CF_2CF_2NS^+$, 100), 119 ($CF_3CF_2^+$, 18.7), 69 (CF_3^+, 93.8), 64 (S_2^+, 3.5). X: 291 ($CF_2ClNNCF_2S_4^+$, 4.1), 259 ($CF_2ClNNCF_2S_3^+$, 5.2), 227 ($CF_2ClNNCF_2^+$, 2.6), 195 ($CF_2ClNNCF_2S^+$, 1.1), 163 ($CF_2ClNNCF_2^+$, 5.8), 128 ($CF_2NNCF_2^+$, 8.6), 85 (CF_2Cl^+, 12.6), 64 (S_2^+, 0.6), 61 ($NCCl^+$, 100). The ^{19}F NMR spectrum of IX showed two singlets at ϕ −88.4 (CF_3) and −116.3 (CF_2) in the ratio of 3:2. A singlet at ϕ −64.6 was obtained in ^{19}F NMR spectrum of $(CF_2ClN)_2S_4$. Anal. Calcd. for $(CF_3CF_2N)_2S_4$: S, 32.48. Found: s, 31.41. Calcd for $(CF_2ClN)_2S_4$: S, 39.14. Found: 40.91.

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η^5 Bonding between Main-Group Elements and Cyclopentadiene Rings: An Xα–Scattered-Wave Study

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SCF-Xα–scattered wave (Xα–SW) calculations have been performed on (η^5-C_5H_5)Li, (η^5-C_5H_5)In, (η^5-C_5H_5)BeH, and (η^5-C_5H_5)BeCl. For each molecule, the HOMO is computed to be a doubly degenerate orbital that is located primarily on the C_5H_5 ring. Lone-pair and σ_{BeX} MO's participate to only a minor extent in interstitial bonding. It is suggested that the electronic structures of these simple molecules are more consistent with a six- than an eight-electron counting procedure. Several ionization energies (IE's) have been computed for all four molecules by using the transition-state method. The computed IE's for (η^5-C_5H_5)In agree with experimental ultraviolet photoelectron spectroscopic (UV PES) data but are in disagreement with previous MO calculations on (η^5-C_5H_5)In and (η^5-C_5H_5)Tl. Likewise, our Xα–SW study of (η^5-C_5H_5)BeCl suggests that the UV PES assignments for this molecule should be revised.

Introduction

Following the discoveries of ferrocene, bis(benzene)chromium, and uranocene, there has been an intense interest in annulene π complexes of the d- and f-block elements. As a consequence, significant progress has been made toward understanding the electronic structures and patterns of stability of these fascinating compounds.[2] Much less, however, is known about the perhapto interaction of main-group elements with carbocyclic ligands. Minkin and Minyaev[3] have suggested that annulene-cap perhapto bonding will be favored when the total number of ring π plus main-group moiety electrons is 8. On the other hand, Schleyer et al.[4] have emphasized the "three-dimensional aromaticity" concept and suggested that the optimum number of interstitial electrons[5] is six. Other important attempts to understand the bonding in such main-group nido compounds include ab initio MO calculations on C_5H_5Li[6] and C_5H_5BeH.[7] At the semiempirical level of theory, Dewar and Rzepa[8] have explored the interaction of BeX moieties with cyclopentadienyl, indenyl, and fluorenyl groups, and Bews and Glidewell[9] have investigated beryllium derivatives of various $(CH)_n$ carbocycles. Beryllium derivatives of the type C_5H_5BeR have also been investigated by the PRDDO method.[10] Some polyhedral carbocations bear a close resemblance to multihapto-bonded main-group systems (vide infra); hence, mention should be made of the ab initio calculations[4,11] on $(C_5H_5)CH^{2+}$. Other carbocations such as $C_6H_5^+$ and the heavier congener $C_5H_5Si^+$ have been investigated by ab initio methods.[4c,12] The EHMO method has been employed to study the analogous tin cation $C_5H_5Sn^+$ and the motion of a CH_2^{2+} fragment across a $C_5H_5^-$ ring.[13,14]

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