very nearly in the plane of each cyclobutadiene ring and no significant puckering occurs which would enable the Fe atom to interact more strongly with the exocyclic carbon. (c) The iron atom shows no large displacement from above the center of the cyclobutadiene ring, and the Fe–C$_{11}$ distances are too large (2.85 and 2.94 Å) to support any significant direct metal–exocyclic carbon interaction (the anchimeric effect). The eight iron–ring carbon distances are close to being equal, suggesting the bond energy remains much the same in each case. (d) The carbon–carbon distances of the cyclobutadiene ring remain close to being equal and similar to those in cyclobutadieneiron tricarbonyl itself.[10] This would further suggest that the extreme structure analogous to structure Ic drawn for the ferrocenyl system is not a correct representation.[5, 9]

We conclude that the major interaction leading to stabilization of the cation involves interaction of a filled metal orbital with the four carbon atoms of the cyclobutadiene ring and, through a $\pi-\pi$ carbon–carbon interaction, electrons are transmitted to the electron-deficient exocyclic carbon atoms. Anchimeric effects are not involved nor can any one particular iron–carbon bond in the initial cyclobutadieneiron linkage be singled out as being used to provide electrons for the stabilization. By analogy the same kind of stabilization is presumed to occur in the ferrocenylcarbinyl cations and the benzylchromium tricarbonyl systems. Attempts to obtain suitable material to test this are being undertaken.

An additional point of interest concerns the nmr spectrum of the cyclobutadienyl carbonium ions. The nmr spectrum of the cation IV (R = H) at 40° (SO$_2$) consists of sharp singlets at τ 2.74, 4.40, and 4.67 of areas 1:2:4, respectively. The unexpected equivalence of all four ring protons ortho to the point of substitution suggested rapid rotation about the carbon–carbon exocyclic bond. The spectrum shows coalescence at 0°, and at −50° the rotation is apparently stopped[11] for the ortho protons now appear as two doublets each of relative area 2 centered at τ 4.63 and 4.77 (J = 9 Hz); the remaining proton absorptions are unchanged, appearing at 2.77 (s, 1 H) and 4.38 (s, 2 H). Similarly, the nmr spectrum of the methyl derivative V (R = CH$_3$) at 40° consists of three sharp singlets at τ 4.33, 4.76, and 8.28 of relative area 2:4:3, respectively, but on cooling to +15° the spectrum coalesces, and at 10° rotation is halted, the spectrum showing absorptions at τ 4.43 (s, 2 H), 4.66 (d, 2 H, J = 9 Hz), 4.78 (d, 2 H, J = 9 Hz), and 8.30 (s, 3 H).

On the other hand the nmr spectra of the phenyl derivative VI (R = C$_6$H$_5$) and the cyclopropyl system VII show nonequivalent ortho protons in the cyclobutadiene ring at all temperatures up to 50°. Rotation about the exocyclic bond was also not observed previously in other simple alkyl derivatives related to VII.[5]

A reasonable explanation for these variations is that the bond order of each exocyclic bond in the biscyclobutadienylcarbinyl cations is considerably lower than that of the monocyclobutadienylcarbinyl cations; the reason the biscyclobutadienylphenyl system VI does not show the rotation at room temperature is possibly due to steric crowding.

Acknowledgment. The authors thank the Robert A. Welch Foundation, the National Science Foundation, and the U. S. Army Research Office (Durham) for financial assistance.

Raymond E. Davis, H. D. Simpson
N. Grice, R. Pettit*
Department of Chemistry, The University of Texas
Austin, Texas 78712

Received July 27, 1971

VI. These three salts crystallize with different packing arrangements, in three different space groups, suggesting that the important structural feature of near-coplanarity of the cyclobutadiene rings with the central plane is probably not attributable to packing effects in the crystal.

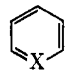
[10] M. I. Davis and C. S. Speed, *J. Organometal. Chem.*, 21, 401 (1970).

[11] Use of an approximative equation (R. J. Karland, M. B. Rubin, and M. B. Wise, *J. Chem. Phys.*, 40, 2426 (1964)) to obtain coalescence temperature rotation rates and the Eyring equation results in the following estimates of the rotational barriers: $\Delta G_{\mathrm{H}}{}^{\ddagger}$ = 13.8 kcal/mol, $\Delta G_{\mathrm{Me}}{}^{\ddagger}$ = 14.7 kcal/mol, $\Delta G_{\mathrm{Ph}}{}^{\ddagger} \gg$ 16.6 kcal/mol (using 50° as a zero-order approximation of the coalescence temperature.)

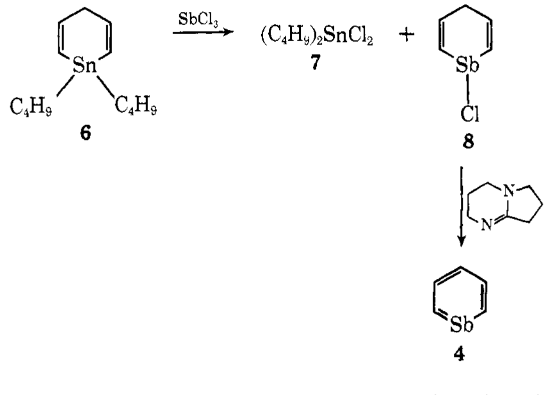
Stibabenzene

Sir:

Multiple bonds to carbon are common for first-row elements but rare outside the first row. A common explanation for the diminished importance of multiple bonds to the heavier atoms is the assumed low strength of such bonds.[1] Our interest in this problem has led us to try to obtain the group V heteroaromatic compounds **1**, **2**, **3**, **4**, and **5**. These compounds would provide a graded series in which carbon is multiply bonded to an entire column of elements and thus should provide detailed information about this bonding as a function of increasing atomic number. The first members of this series, pyridine (**1**), phosphabenzene (**2**),[2] and arsabenzene (**3**),[2] are now available. This communica-



1, X = N
2, X = P
3, X = As
4, X = Sb
5, X = Bi



---

[1] To be more correct it has been estimated that single bonds are much stronger than multiple bonds. This may be true but it is necessary to couple this with the kinetic argument that these multiple bonds would be highly reactive in order to explain the rarity of such species. See: K. S. Pitzer, *J. Amer. Chem. Soc.*, 70, 2140 (1948); R. S. Mulliken, *ibid.*, 72, 4493 (1950); D. E. Douglas and D. H. McDaniel, "Concepts and Models of Inorganic Chemistry," Ginn, New York, N. Y., 1965, p 58; R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, New York, N. Y., 1965, pp 3, 8–10, 20.

[2] A. J. Ashe, III, *J. Amer. Chem. Soc.*, 93, 3293 (1971).

tion describes the synthesis of the fourth compound, stibabenzene (antimonin) (**4**).

1,4-Dihydro-1,1-dibutylstannabenzene (**6**)[3] and antimony trichloride reacted exothermally in a THF solution. Distillation gave a waxy crystalline mixture of dibutyltin dichloride (**7**) and 1,4-dihydro-1-chlorostibabenzene (**8**). Recrystallization from heptane afforded pure **8**, mp 115–117° dec. The pmr spectrum[4] ($CDCl_3$) showed a two-proton diallylic multiplet at τ 6.6 and the four vinylic protons as an AB pattern (J_{AB} = 13 Hz) at 3.5 and 3.1 [each peak was split into a triplet (J_{AC} = 3.5 Hz and J_{BC} = 2 Hz, respectively)]. It is convenient to treat a solution of the crude mixture of **7** and **8** in tetraglyme with 1,5-diazabicyclo[4.3.0]non-5-ene to produce stibabenzene. Compound **4** may be isolated by vacuum distillation into a Dry Ice cooled receiver. Stibabenzene is an extremely labile compound and rapidly polymerizes to an intractable brown tar at −80°. Handling appears most convenient in a dilute solution under an inert atmosphere although even these solutions slowly precipitate the brown polymer.

The pmr spectrum of stibabenzene in Figure 1 shows the characteristic pattern of the group V heteroaromatics. The α protons occur as a doublet (J = 11 Hz) at extremely low field while the β and γ protons are in the normal aromatic region. The chemical shift of the α protons is τ 1.9 for pyridine, 1.4 for phosphabenzene, 0.7 for arsabenzene, and −0.7 for stibabenzene. This progressive shift to lower field can probably be associated with the magnetic anisotropy of the increasing large heteroatom.[5] This effect should be attenuated for the more remote β and γ protons and indeed chemical-shift values of these protons do not vary greatly for **1**, **2**, **3**, and **4**. These low-field chemical-shift values are consistent with an appreciable ring current for **1**, **2**, **3**, and **4**.[6]

The mass spectrum of stibabenzene (Table I) like that of **1**, **2**, and **3** shows the molecular ion as the base peak. Also, like **1**, **2**, and **3**, as well as benzene,[7] stibabenzene shows significant fragmentation by loss of acetylene. However, there are some important differences as well. Stibabenzene shows large peaks due to the metal atom[8] as well as from loss of the metal atom.

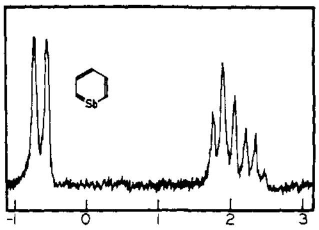


Figure 1. Proton magnetic resonance spectrum of stibabenzene. The spectrum was determined at 60 MHz. τ values are in parts per million relative to internal TMS.

Table I. Mass Spectrum of Stibabenzene Showing Major Ions and Their Relative Abundances[a]

Ion (m/e)	Rel abundance	Assignment
188	65	$(C_5H_5{}^{123}Sb)^+$
186	100	$(C_5H_5{}^{121}Sb)^+$
162	9	$(P - C_2H_2)^+$
160	16	$(P - C_2H_2)^+$
123	17.5	$({}^{123}Sb)^+$
121	27	$({}^{121}Sb)^+$
65	95	$(P - Sb)^+$
39	95	$(C_3H_3)^+$

[a] The mass spectra were determined on an MS-9 spectrometer at 45 eV using a gas inlet.

The uv spectrum of stibabenzene (cyclohexane) has intense bands at 236 and 312 mμ.[9] These appear to correspond to the intense bands in the spectra of phosphabenzene at 213 and 246 mμ and of arsabenzene at 219 and 268 mμ. If these bands are due to $\pi \rightarrow \pi^*$ transitions, they can be associated with a smaller separation of the bonding and the antibonding energy levels for the heavier heteroaromatics and hence to weaker bonding in stibabenzene relative to arsabenzene and phosphabenzene.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant No. 5241-AC3-4) and also the National Science Foundation for a grant (GP-8345) to the University of Michigan for the purchase of an MS-9 mass spectrometer. Thanks are also due to Miss Joann Schmidt for help in preparing compound **6**.

---

(3) A. J. Ashe, III, and P. Shu, *J. Amer. Chem. Soc.*, **93**, 1804 (1971).

(4) The pmr spectra were taken in dilute solutions of the indicated solvent using TMS as an internal standard. They were recorded using a Varian T-60 instrument. The mass spectra were taken on an AEI Model MS-9 spectrometer at 45 eV using a gas inlet. The uv spectra were recorded in cyclohexane using balanced 1-cm cells on a Cary-14 spectrometer.

(5) For pyridine see: J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc., London*, 303 (1961).

(6) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961), and for a brief summary see G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge, England, 1969, pp 61–70.

(7) E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, "Atlas of Mass Spectral Data," Vol. 1, Interscience, New York, N. Y., 1969, p 101, 102.

(8) There are few reported mass spectra of stibines for comparison. However, trimethylstibine also shows a large antimony peak: R. E. Winter and R. W. Kiser, *J. Organometal. Chem.*, **10**, 7 (1967).

(9) The extinction coefficients for these bands are approximately 10^4. The facile polymerization of **4** makes an exact determination of ϵ difficult.

Arthur J. Ashe, III
Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48104
Received September 2, 1971

Nature of Sulfur Species in Fused Salt Solutions[1]

Sir:

A brilliant blue color develops in liquid potassium thiocyanate when it is heated above 300°.[2] Liquid LiCl-KCl eutectic in contact with sulfur also acquires a deep blue coloration.[3] Absorption spectra of the blue thiocyanate and alkali halide melts were found to be virtually identical and the band at 17,000 cm^{-1} giving rise to the blue color was originally thought to be due to a neutral sulfur species, possibly S_2 molecules.[3,4]

By combining electrochemical with spectrophotometric measurements, Bodewig and Plambeck[5] were

---

(1) Work performed under the auspices of the U. S. Atomic Energy Commission and the Environmental Protection Agency.

(2) (a) C. Nöllner, *Pogg. Ann.*, **98**, 189 (1856); (b) E. Paternó and A. Mazzuchelli, *Gazz. Chim. Ital.*, **38**, 137 (1908).

(3) J. Greenberg, B. R. Sundheim, and D. M. Gruen, *J. Chem. Phys.*, **29**, 461 (1958).

(4) H. Lux and H. Anslinger, *Chem. Ber.*, **94**, 1161 (1961).

(5) F. G. Bodewig and J. A. Plambeck, *J. Electrochem. Soc.*, **116**, 607 (1969); **117**, 904 (1970).