The ^{11}B nmr spectra of I and II are reminiscent of those of decaborane(14) derivatives. The spectrum (32.1 MHz, $BF_3 \cdot OEt_2$ as reference) of I consists of a multiplet of two overlapping doublets (determined by decoupling ^1H) at -11.8 and -9.2 ppm (relative intensity of approximately 2:2), a doublet at 0.9 ppm (intensity 3), and two small doublets (both intensity 1) at 27.4 and 34.3 ppm. The spectrum of II was similar at low field with less well resolved doublets at -9.0, -6.9, and 2.9 ppm (overall intensity 8) and a single high-field doublet at 36.5 ppm (intensity 1). Coupling constants, where resolved, were similar to those of decaborane(14) derivatives. The ^1H nmr spectra of I and II were quite similar, containing five overlapping sets of quartets at $\tau \sim 6$ to 12 (BH terminal, determined by decoupling ^{11}B), a single broad peak at $\tau \sim 13.5$ (B–H–B), and a similar broad peak at $\tau \sim 21.4$ (Mn–H–B). The complexed THF in II was readily identified.

The crystal and molecular structure of II has been determined by single-crystal X-ray techniques. The compound crystallizes in space group $P\bar{1}$ with lattice constants $a = 12.866$ (23), $b = 9.792$ (21), $c = 7.183$ (13) Å; α 90.21 (6), $\beta = 108.12$ (6), $\gamma = 104.48$ (6)°. There are two molecules in the unit cell. The intensity data were collected by using a FACS-I diffractometer, at room temperature, using Mo Kα radiation. A complete sphere of data bounded by $2\theta = 45°$ was collected. All the atomic positions were located by Patterson and Fourier techniques, and full-matrix refinement of 1363 observed reflections provided conventional and weighted R values of 3.4 and 4.1%, respectively. The structure is shown in Figure 1.

Representative angles and distances around the manganese atom in II are listed in Table I. The angles and distances in the remainder of the B_9 cage are very similar to those in $B_{10}H_{14}$.[1] The spectroscopic similarities of I and II suggest that they possess identical metalloborane cage arrangements. This similarity has been further verified by a preliminary crystallographic investigation of the potassium salt of I.

Table I. Selected Interatomic Distances and Angles in $Mn(CO)_3[B_9H_{12}(OC_4H_8)]$ (II)

Angles, deg		Distances, Å	
H_1–Mn–H_4	93.45 (2.30)[a]	Mn–C_3	1.793 (5)
H_1–Mn–C_3	91.32 (1.46)	Mn–H_1	1.75 (4)
H_1–Mn–C_2	175.70 (1.48)	B_5–H_1	1.24
C_1–Mn–C_2	90.10 (18)	Mn–B_5	2.237 (5)
C_1–Mn–C_3	91.11 (23)	Mn–B_2	2.196 (6)
B_2–Mn–C_3	161.38 (07)	B_2–O_4	1.526
B_2–Mn–H_1	77.52 (1.45)		

[a] Standard deviations.

A unique feature of these new metalloboranes is their high thermal, hydrolytic, and oxidative stability compared to that of other metalloboranes.[2] This stability is undoubtedly related to unusual bonding of the metal to the borane cage. The B_9 moiety can be considered to be tridentate and is formally a five-electron donor bound to the Mn by two three-center two-electron hydrogen bridge bonds (that contribute a total of three electrons to the metal) and a single boron–metal bond [Mn–B(2)] (that contributes two electrons to the metal). It has been suggested that the B_9 moiety in *trans*-$[(C_2H_5)_3P]_2PtB_9H_{11}L$[3] is effectively a bidentate ligand. The evidence at hand indicates that these latter compounds are most likely not related, in a bonding sense, to the compounds reported here.

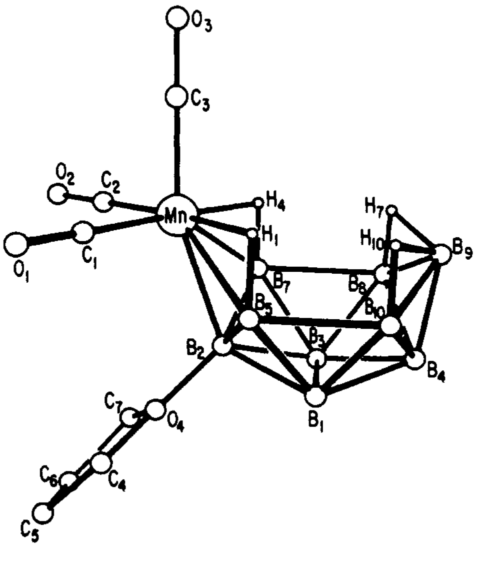


Figure 1. The structure of $Mn(CO)_3[B_9H_{12}(OC_4H_8)]$. Terminal hydrogens on C_4–C_7, B_1, and B_8–B_{10} have been omitted for clarity.

Under selected photolytic conditions it has been possible to exchange triphenylphosphine ligands for several of the CO ligands on I and II and also for the complexed tetrahydrofuran on the covalent species II. Attempts to displace THF using amines results in a more complex reaction that is described elsewhere.[4]

The chemistry of these compounds and other transition metal derivatives of $B_9H_{14}^-$ is under investigation and will be more fully reported later.

Acknowledgment. This work has been supported in part by grants from the National Science Foundation and the Office of Naval Research.

---

(1) J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Crystallogr.*, 3, 436 (1950).

(2) For examples, see E. L. Muetterties, *Pure Appl. Chem.*, **29**, 585 (1972); L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 5665 (1972).

(3) A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 2571 (1970).

(4) D. F. Gaines, J. W. Lott, and J. Calabrese, *J. Chem. Soc., Chem. Commun.*, in press.

J. W. Lott, D. F. Gaines*
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
H. Shenhav, R. Schaeffer
Department of Chemistry, Indiana University
Bloomington, Indiana 47401

Received January 27, 1973

Diaminocyclopropenones and Diaminocyclopropenethiones. Quasi-urea and Quasi-thiourea

Sir:

The highly strained, smallest ring systems having heterosubstituents are of considerable interest from organic and theoretical viewpoints. As has been re-

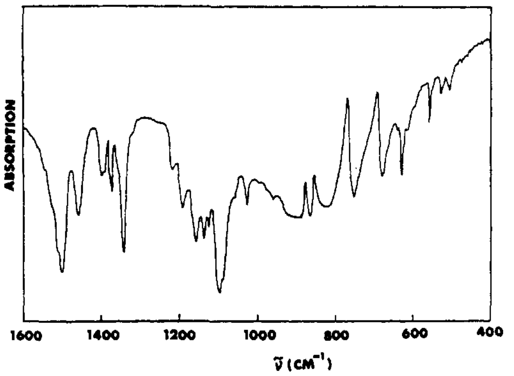
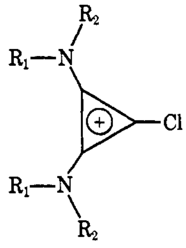


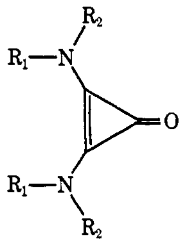
Figure 1. Infrared spectrum of **4**.

ported in our previous work,[1] the amino substituents do dramatically stabilize the cyclopropenium cation. Breslow and his coworkers have stated the strong conjugative interaction between amino group and cyclopropenone ring in 1-phenyl-2-diethylaminocyclopropenone.[2] These works prompted us to find synthetic pathways to new electronic systems of diaminocyclopropenones and diaminocyclopropenethiones and to investigate their novel physicochemical properties. Here, we wish to report facile preparative methods of these ketones and thiones and to discuss briefly their spectroscopic characteristics.

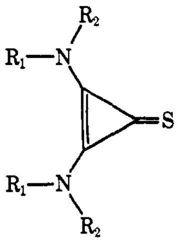
To a methanol solution of 1,2-bis(diisopropylamino)-3-chlorocyclopropenium perchlorate[1] (**1a**) was added a solution of 5% aqueous potassium hydroxide, and the solution was stirred for 3 hr. The reaction mixture was extracted with carbon tetrachloride. After removal of solvent, sublimation under reduced pressure gave colorless needles (**2a**) in 80% yield, mp 210°. *Anal.* Calcd for $C_{15}H_{28}N_2O$: C, 71.38; H, 11.18; N, 11.10; O, 6.34. Found: C, 71.64; H, 11.12; N, 11.03; O, 6.47. The mass spectrum shows a parent ion at *m/e* 252. The characteristic ir absorptions for cyclopropenone ring[3] were observed at 1902, 1857, and 1578 cm^{-1}. The lowest frequency band among them is strongly coupled with the C–N stretching vibration. The ketone, **2a**, is quite stable. As a matter of fact, no changes have been observed even in 25% hot KOH aqueous solution. The ultraviolet spectrum of **2a** in CH_3CN exhibits λ_{max} 230 nm (log ϵ 4.16) with a shoulder at 260 (3.36). The nmr spectrum ($CDCl_3$) shows equivalent isopropyl groups, a doublet at τ 8.70 (24 H) and a sesquitet at 6.36 (4 H). Since 1-phenyl-2-diethylaminocyclopropenone shows two different chemical shifts of ethyl groups,[2] the lowered rotational barrier around the C–N bonds of **2a** might be responsible for equivalency of the four isopropyl groups due to the decreased π conjugation between the amino groups and the cyclopropenone ring by introduction of a second amino group.



1



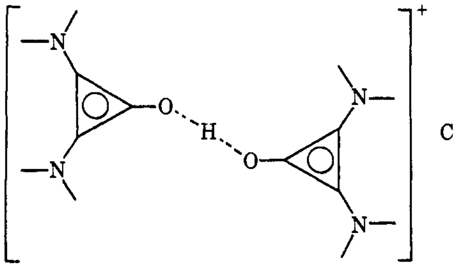
2



3

a, $R_1 = R_2 = i\text{-Pr}$
b, $R_1 = t\text{-Bu}$; $R_2 = \text{Me}$

It is particularly interesting to note that treatment of **2a** with perchloric acid resulted in formation of a colorless adduct (**4**) with two ketones and one acid, mp 185° (dec). *Anal.* Calcd for $C_{30}H_{57}N_4O_6Cl$: C, 59.53; H, 9.49, N, 9.26, O, 15.86, Cl, 5.86. Found: C, 59.70, H, 9.90, N, 9.26, O, 15.83, Cl, 5.91. Nmr ($CDCl_3$) τ −3.74 (singlet, 1 H), 6.26 (sesquitet, 8 H), and 8.70 (doublet, 48 H). Treatment of the adduct **4** with aqueous potassium hydroxide readily reproduced **2a**. The ir spectrum of **4** shows strong bands at 1500 and 1098 cm^{-1} and broad background absorption (Figure 1) in the region from 1200 to 500 cm^{-1} with a maximum absorption at around 900 cm^{-1}. The ordinary O–H stretching vibration has never been observed above 1600 cm^{-1} for **4**. The characteristic broad absorption is assigned to the asymmetric stretching vibration of O–H–O.[4] Such an extraordinary phenomenon in the infrared spectrum has been encountered in the strong hydrogen bond system, *i.e.*, acid adducts of acetamide,[5] urea,[6] and 1-methyl-2-quinolinone.[4b] Therefore, the structure of **4** seems to be akin to cyclopropenium ion rather than cyclopropenone as is shown below.



4

Treatment of a methanol solution of **1a** with 2% aqueous sodium sulfide immediately gave a white precipitate. Sublimation under reduced pressure afforded bis(diisopropylamino)cyclopropenethione (**3a**) in 80% yield, mp 258°. *Anal.* Calcd for $C_{15}H_{28}N_2S$: C, 67.11, H, 10.51, N, 10.43, S, 11.95. Found: C, 67.23, H, 10.23; N, 10.57; S, 12.04; *m/e* 268. The ir spectrum of **3a** shows a weak band at 1852 cm^{-1} assigned to the characteristic ring skeletal vibration of cyclopropenethione;[7] nmr ($CDCl_3$) τ 8.59 (doublet, 24 H), 6.18 (sequitet, 4 H); uv (CH_3CN) λ_{max} 271 nm (log ϵ 4.25), 234 (4.14). Thione **3a** also resists alkaline hydrolysis. It is noteworthy that the reaction of **3a** with alkylating reagents occurs at the sulfur atom to yield the corresponding diaminomercaptocyclopropenium salts (**5**). For example, reaction of **3a** with

---

(1) Z. Yoshida and Y. Tawara, *J. Amer. Chem. Soc.*, **93**, 2573 (1971).

(2) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1326 (1965).

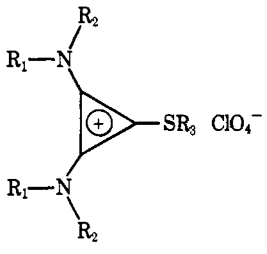
(3) (a) A. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 10 (1965); (b) G. L. Closs, *Advan. Alicyclic Chem.*, **1**, 53 (1966).

(4) (a) A. L. Macdonald, J. C. Speakman, and D. Hadži, *J. Chem. Soc., Perkin Trans.*, *2*, 825 (1972); (b) M. Calleri and J. C. Speakman, *J. Chem. Soc. A*, 1644 (1969).

(5) N. Albert and R. M. Badger, *J. Chem. Phys.*, **29**, 1193 (1958).

(6) (a) R. Mecke and W. Kutelnigg, *Chem. Ber.*, **94**, 1706 (1961); (b) A. Luttringhaus and H. W. Dirksen, *Angew. Chem.*, **75**, 1059 (1963).

(7) Y. Kitahara and M. Funamizu, *Bull. Chem. Soc. Japan*, **37**, 1897 (1964).



5

methyl iodide in benzene and successive treatment with aqueous $KClO_4$ solution gave colorless crystals of 1,2-bis(diisopropylamino)-3-methylthiocyclopropenium perchlorate (**5a**, $R_1 = R_2 =$ *i*-Pr, $R_3 =$ Me) quantitatively, mp 157°. The prominent ir bands of **5a** appear at 1899 and 1547 cm^{-1}; uv (MeOH) λ_{max} 266 nm (log ϵ 3.91), 214 (4.02); nmr ($CDCl_3$) τ 8.62 (doublet, 24 H), 7.24 (singlet, 3 H), 6.02 (sequitet, 4 H). Di-*tert*-butylmethylaminocyclopropenone (**2b**) and the corresponding thione (**3b**) were obtained by similar procedures in moderate yield.

It has been reported that tetramethylurea forms a stable acid adduct formulated as $((CH_3)_4N_2CO)_2 \cdot HSbCl_6$.[6b] One can point out a striking similarity of **2** to tetraalkylurea in the chemical behavior. The reaction of **3a** with methyl iodide (electrophile) is also similar to the corresponding reaction of thioureas. These chemical properties are explainable if we assume that the three-membered ring corresponds to a sp^2 carbon atom. In this sence, we can call diaminocyclopropenones and diaminocyclopropenethiones quasi-urea and quasi-thiourea, respectively.

Z. Yoshida,* H. Konishi, Y. Tawara, H. Ogoshi
Department of Synthetic Chemistry, Kyoto University
Yoshida, Kyoto 606, Japan
Received February 20, 1973

Matrix Raman Spectrum of the Fluorine Molecular Anion, F_2^-

Sir:

As early as 1955, Känzig[1] postulated the existence of F_2^- as observed in the electron spin resonance spectrum of γ-irradiated crystalline LiF at 77°K. In later work, Delbecq, *et al.*,[2] reproduced the Känzig results on F_2^- while Vande Kieft and Gilliam[3] produced the F_2^- species by irradiating alkali bifluoride salts $M^+HF_2^-$. Balint-Kurti and Karplus[4] have performed potential energy surface calculations for the reaction $Li + F_2 \rightarrow LiF + F$. Even though this reaction is exothermic by approximately 100 kcal/mol, there is a stable complex intermediate, isosceles triangular $Li^+F_2^-$, which has a maximum calculated well depth of approximately 40 kcal/mol.

In view of the potentially limited stability of the $M^+F_2^-$ species, argon matrix reactions of alkali metal atoms and fluorine molecules were used to produce and isolate this reaction product. Fluorine samples in argon (Ar/F_2 = 50 and 100) were deposited on a tilted copper wedge maintained near 15°K. An atomic beam of alkali metal was codeposited with the fluorine sample using metal vapor pressures near 1 μ. The experimental technique and spectroscopic and cryogenic equipment have been described previously.[5,6] Raman spectra from 50 to 1100 cm^{-1} were recorded using approximately 100 mW of 4880 and 5145 Å excitation from the argon plasma laser. Band positions were determined by calibration with argon fluorescence lines which were superimposed on the spectra during the running scan.

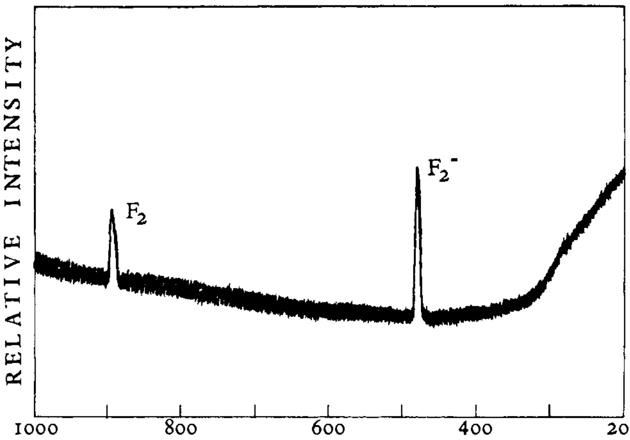


Figure 1. Raman matrix spectrum of fluorine (Ar/F_2 = 50) reacting with sodium atoms. Instrumental parameters: exciting line approximately 100 mW of 4880 Å; range, 0.3×10^{-9} Å; filter, 5-Å dielectric spike; rise time, 3 sec; scan speed, 10 cm^{-1}/min.

The Raman spectra of alkali metal atom–F_2 matrix reaction products showed only two bands, one at 892 ± 1 cm^{-1} due to F_2 in excellent agreement with the gas-phase value[7] and the other near 460 cm^{-1} depending on the particular alkali metal reagent. No metal fluorides (M^+F^-) were observed in the Raman spectrum owing to the very low Raman intensities of such ionic species. Argon matrix frequencies[8] of LiF, NaF, and KF are accurately known; these spectral regions were void of signal.

Figure 1 shows the spectrum of the sodium–F_2 reaction products. Here the new band appeared at 475 ± 1 cm^{-1}. This feature exhibited instability due to laser photolysis; 10 min of laser illumination decreased the band intensity by approximately one-half. Furthermore, the intensity ratio of the 892 cm^{-1} feature to the 475-cm^{-1} band *increased* during laser illumination as the lower feature was photodecomposed faster by the laser than F_2 itself. In lithium experiments, the new feature was observed at 452 ± 1 cm^{-1}, 464 ± 1 for K, 462 ± 1 for Rb, and at 459 ± 1 cm^{-1} for Cs. Clearly, the alkali metal is associated with the new species producing the Raman signal near 460 cm^{-1}.

Due to the photolytic instability of the new product species, depolarization ratio measurements were difficult to make. However, in the sodium case the 475-cm^{-1} band had sufficient intensity to record depolarization data; an average ratio of 0.7 was obtained for the 475-cm^{-1} band. The same depolarization ratio

---

(1) W. Känzig, *Phys. Rev.*, **99**, 1890 (1955).

(2) C. J. Delbecq, W. Hayes, and P. H. Yuster, *Phys. Rev.*, **121**, 1043 (1961).

(3) L. J. Vande Kieft and O. R. Gilliam, *Phys. Rev. B*, **1**, 2015 (1970).

(4) G. G. Balint-Kurti and M. Karplus, *Chem. Phys. Lett.*, **11**, 203 (1971); *J. Chem. Phys.*, **50**, 478 (1969).

(5) D. A. Hatzenbuhler and L. Andrews, *J. Chem. Phys.*, **56**, 3398 (1972).

(6) L. Andrews, *J. Chem. Phys.*, **57**, 51 (1972).

(7) D. Andrychuk, *J. Chem. Phys.*, **18**, 233 (1950).

(8) L. Andrews and J. I. Raymond, *J. Chem. Phys.*, **55**, 3078 (1971).