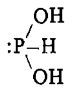
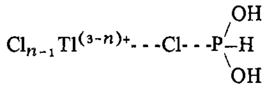


is a better electron donor. Formation of an activated complex



may find support from the fact that a similarly bridged complex $Cl_3Tl\cdots Cl\cdots Cl_2PO$ has been considered to be a possibility in chloride-exchange kinetics between $TlCl_3$ and $POCl_3$.[40]

The mechanism on the basis of an active form of hypophosphorous acid[39] could be

$$H_3PO_2(\text{normal}) \overset{K_d}{\rightleftharpoons} H_2PO_2^- + H^+ \quad (\text{rapid}) \tag{12}$$

$$H_3PO_2(\text{normal}) + H^+ \xrightarrow{k_a} H_3PO_2(\text{active}) + H^+ \quad (\text{slow}) \tag{13}$$

$$H_3PO_2(\text{active}) + H^+ \xrightarrow{k_a} H_3PO_2(\text{normal}) + H^+ \quad (\text{rapid}) \tag{14}$$

$$H_3PO_2(\text{active}) + TlCl_n{}^{3-n} \xrightarrow{k_n} \text{products} \quad (\text{slow}) \tag{15}$$

Assuming a steady state for H_3PO_2(active), rate law (16) is

$$\frac{-d[Tl(III)]}{dt} = \frac{k_nK_dk_a[Tl(III)]_T[H^+]^2[H_3PO_2]_T}{([H^+] + K_d)(k_a'[H^+] + k_n[Tl(III)])} \tag{16}$$

obtained. If $k_a'[H^+] \gg k_n[Tl(III)]$, the rate law (16) reduces to (17). This is same as the experimental rate law (5) with

$$\frac{-d[Tl(III)]}{dt} = \frac{k_nK_dk_a}{k'_a}\,\frac{[H^+][Tl(III)]_T[H_3PO_2]_T}{[H^+] + K_d} \tag{17}$$

$k'_{obsd} = k_nK_dk_a/k_a'$.

For Tl(III)-Tl(I) exchange reaction it has been shown that the reaction is decelerated by small amounts of chloride,[3-5] bromide,[11] and cyanide[12] ions but strongly accelerated by larger amounts. It has been concluded that the species $TlCl^{2+}$, $TlBr^{2+}$, and $TlCN^{2+}$ are least reactive. In the present investigation, too, the overall rate appears to decrease with the increase in chloride ion until $R \simeq 1$. This may suggest $TlCl^{2+}$ to be least reactive (Table IV).

In contrast is the oxidation of 1,2-cyclohexanedione[6] in which the $TlCl^{2+}$ species has been reported to be most reactive, *i.e.*, more reactive than Tl^{3+}, $TlOH^{2+}$, and higher chloro complexes. The opposite role of $TlCl^{2+}$ in the two oxidations probably indicates that the two reactions occur through entirely different mechanisms.

It appears that $TlCl^{2+}$ is less reactive than aquothallic ion because chloride inhibits the formation of an intermediate complex of Tl^{3+} and H_3PO_2 and at the same time the thallium(III) reduction does not occur *via* a bridged activated complex. This probably becomes operative with the formation of $TlCl_2^+$ and subsequent complexes.

Two implications are thus obvious: (1) chloride ions inhibit the formation of intermediate complexes in all cases and (ii) chloride ions accelerate the redox processes in those cases where a bridge-activated mechanism can operate.

Registry No. Tl^{3+}, 14627-67-9; $TlCl^{2+}$, 23715-56-2; $TlCl_2^+$, 23172-38-5; $TlCl_3$, 13453-32-2; $TlCl_4^-$, 18616-42-7; H_3PO_2, 6303-21-5; Cl^-, 16887-00-6.

---

[40] J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 1305 (1963).

Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48824

Microwave Spectrum, Barrier to Internal Rotation, Dipole Moment, and Molecular Structure of Methyldifluorophosphine[1,2]

EDWARD G. CODDING, ROBERT A. CRESWELL, and R. H. SCHWENDEMAN*

Received July 23, 1973

The microwave spectrum of methyldifluorophosphine has been assigned in the ground state and the three lowest excited vibrational states. From the splittings of the ground and first excited torsional states the barrier to the methyl group internal rotation was found to be 2300 (50) cal/mol. Stark effect measurements gave the following values for the dipole moment and its components: $\mu_a = 2.047$ (2) D, $\mu_b = 0.0$ D, $\mu_c = 0.195$ (62) D, and $\mu = 2.056$ (6) D. With judicious assumptions for the methyl group geometry and the PF bond length, the PC bond length was found to be 1.82 Å.

Introduction

A study of methyldifluorophosphine was undertaken as a result of recent interest in difluorophosphine derivatives in our laboratory and elsewhere.[3-7] Determination of the barrier to internal rotation of the methyl group would provide an interesting comparison to the previously reported values for methylphosphine,[8] methylamine,[9] methyl-

---

[1] This work was supported in part by grants from the National Science Foundation.

[2] A preliminary account of this work was presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1971.

[3] A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, 93, 6772 (1971).

[4] A. H. Brittain, J. E. Smith, and R. H. Schwendeman, *Inorg. Chem.*, 11, 39 (1972).

[5] P. L. Lee, K. Cohn, and R. H. Schwendeman, *Inorg. Chem.*, 11, 1917 (1972).

[6] E. G. Codding, C. E. Jones, and R. H. Schwendeman, *Inorg. Chem.*, 13, 178 (1974).

[7] R. L. Kuczkowski, *J. Amer. Chem. Soc.*, 90, 1705 (1968).

[8] T. Kojima, E. L. Breig, and C. C. Lin, *J. Chem. Phys.*, 35, 2139 (1961).

[9] T. Itoh, *J. Phys. Soc. Jap.*, 11, 264 (1956); D. R. Lide, Jr., *J. Chem. Phys.*, 27, 343 (1957).

difluoramine,[10] and methyldifluoroarsine.[11] In addition, structural information could be compared to the previously reported bond lengths and bond angles in similar molecules.

Experimental Section

The sample of methyldifluorophosphine was obtained from Dr. K. Cohn and used as received. The spectra were taken at about 220 K and at room temperature using both Hewlett-Packard 8460A and conventional laboratory-constructed spectrometers. A far-infrared spectrum of CH_3PF_2 in the gas phase was taken in the 250-450-cm^{-1} region with a Block Engineering FTS-16 Fourier transform spectrometer.

Spectrum

A projection of the molecule in the *ac* plane is shown in Figure 1. Trial rotational constants were calculated from the structure given by selection of parameters from related molecules.[3-7] Both the predicted and observed spectra were quite rich, the predicted spectrum being dominated by c-type Q-branch transitions. Guided by the trial calculations the $0_{00}-1_{01}$ and $1_{11}-2_{12}$ transitions were assigned from which values for the B and C rotational constants were derived. The assignment was completed by finding the A-dependent $1_{01}-2_{02}$ and $1_{01}-2_{20}$ transitions.

Close examination of the $3_{03}-4_{04}$, $3_{13}-4_{14}$ doublet showed it to be composed of six closely spaced lines. Their assignment proved to be the $3_{03}-4_{04}$ and $3_{13}-4_{14}$ transitions involving levels of both A and E internal rotation symmetry and the $3_{13}-4_{04}$ and $3_{03}-4_{14}$ "forbidden" transitions involving E levels. These six frequencies were measured by digital recording and least-squares fitting to a sum of six Lorentzian line shapes. A similar effect was observed in the $5_{05}-5_{24}$, $5_{15}-5_{14}$ doublet. These splittings indicated that the barrier to internal rotation of the methyl group is about 2300 cal/mol.

Each low-J ground-state transition was accompanied by three nearby satellite transitions. These were assigned to the first excited torsional state, ν_t, and to two other low wave number vibrations, ν_a and ν_b. The far-infrared spectrum was recorded from 250 to 450 cm^{-1} and shows two bands centered at 325 and 408 cm^{-1}. The relative intensities in the microwave spectrum indicate that these correspond to ν_a and ν_b, respectively.

The observed transition frequencies and the deviations from the least-squares fits are listed in Table I. The rotational constants, moments of inertia, and internal rotation parameters are given in Table II. Several attempts were made to assign transitions in the ^{13}C species in natural abundance. Although some transitions which appear to belong to the ^{13}C species were examined, no consistent assignment could be made. The difficulty is one of overlapping lines rather than sensitivity, since the observed transitions were recorded with good signal-to-noise ratio.

Stark Effect

A comparison of observed and calculated Stark shifts for four ground-state transitions is given in Table III. The calculated slopes were obtained with $\mu_a = 2.047$ D, $\mu_b = 0.0$ D, and $\mu_c = 0.195$ D. Removal of the constraint on μ_b alters μ_a and μ_c slightly and gives $\mu_b^2 = -0.006$ D^2 thus supporting our assumption of C_s symmetry. The dipole moment vector makes an angle of 5.5 (1)° with the *a* principal axis. Although the sign of this angle and the direction of the dipole moment vector are not determined by the data, the orientation is most likely that shown in Figure 1.

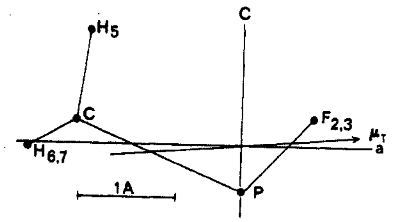


Figure 1. Projection of CH_3PF_2 in its *ac* plane of symmetry showing the orientation of the dipole moment vector. The dipole moment vector points from plus to minus charge.

Table I. Comparison of Observed[a] and Calculated[b] Frequencies of Rotational Transitions in Methyldifluorophosphine.

Transition	Ground state	$v_a = 1$	$v_b = 1$
$0_{00}-1_{01}$	11,179.90 (0.11)		
$1_{01}-2_{02}$	20,216.04 (0.08)	20,154.51 (0.07)	20,239.74 (0.03)
$1_{11}-2_{12}$	19,908.95 (0.08)	19,839.71 (−0.03)	19,932.75 (0.11)
$1_{10}-2_{11}$	24,810.36 (0.07)	24,797.17 (0.01)	24,815.46 (−0.04)
$1_{01}-2_{20}$	30,765.05 (0.06)		
$2_{02}-3_{03}$			28,859.74 (0.08)
$2_{12}-3_{13}$	28,788.33 (0.05)	28,674.26 (−0.01)	28,828.66 (0.10)
$2_{11}-3_{12}$	34,396.54 (−0.14)	34,355.29 (0.01)	
$2_{21}-3_{22}$	33,539.24 (−0.14)		
$2_{20}-3_{21}$			
$3_{03}-4_{04}$	37,532.78 (−0.20)		37,589.76 (−0.08)
$3_{13}-4_{14}$	37,530.92 (−0.14)		37,587.84 (−0.07)

Ground-State Torsional Splittings

Transition	ν_A	ν_E	$\nu_E{}^{*c}$	$\nu_A - \nu_E{}^c$
$3_{13}-4_{14}$	37,530.920	37,531.123		−0.203 (−0.028)
$3_{03}-4_{04}$	37,532.778	37,532.529		0.249 (−0.026)
$3_{03}-4_{14}$			37,533.174	0.396 (−0.003)
$3_{13}-4_{04}$			37,530.491	−0.429 (−0.009)
$5_{15}-5_{14}$	23,517.35	23,516.80		0.55 (−0.03)
$5_{05}-5_{24}$	23,518.22	23,518.64		−0.42 (−0.02)
$5_{05}-5_{14}$			23,517.57	−0.22 (−0.02)
$5_{15}-5_{24}$			23,517.85	0.37 (−0.01)

First Excited Torsional State

Transition	ν_A	ν_E	$\nu_A - \nu_E$
$1_{10}-2_{11}$	24,735.04 (0.15)	24,735.04	0.00 (0.01)
$1_{11}-2_{12}$	19,867.47 (0.10)	19,869.66	−2.19 (0.04)
$1_{01}-2_{02}$	20,195.23 (0.07)	20,194.53	0.70 (−0.02)
$1_{01}-2_{20}$	30,738.92 (0.05)	30,742.93	−4.01 (−0.01)
$2_{20}-3_{21}$	38,123.14 (−0.08)	38,122.30	0.84 (0.00)
$2_{21}-3_{22}$	33,451.68 (−0.02)	33,452.54	−0.86 (0.07)
$2_{11}-3_{12}$	34,361.14 (−0.11)	34,363.30	−2.16 (−0.01)
$2_{12}-3_{13}$	28,744.41 (−0.01)	28,755.39	−10.98 (0.03)
$2_{02}-3_{03}$	28,780.15 (−0.02)	28,771.07	9.08 (0.07)

[a] In MHz. Estimated uncertainties are ±0.05 MHz. [b] Values in parentheses are observed minus calculated frequencies in MHz. [c] $\nu_E{}^*$ is the frequency of a normally forbidden transition between E levels. For the forbidden lines $\nu_A - \nu_E$ is the frequency separation from the nearest A transition.

The dipole moment of CH_3PF_2 (2.056 (6) D) is compared with values obtained for several related compounds in Table IV.

Molecular Structure

With the assumption of a plane of symmetry and a symmetric, untilted methyl group, seven parameters are required to specify the structure of CH_3PF_2. Since we have inertial data on only one isotopic species, three parameters may be determined if we make four assumptions. We have chosen the orientation of the methyl group to be that shown in Figure 1 and $r(CH) = 1.093$ Å and $\angle(PCH) = 109.7°$. For the other necessary assumption we have chosen the PF

---

(10) L. Pierce, R. G. Hayes, and J. F. Beecher, *J. Chem. Phys.*, 46, 4352 (1967).

(11) L. J. Nugent and C. D. Cornwall, *J. Chem. Phys.*, 37, 523 (1962).

Table II. Inertial Constants and Internal Rotation Parameters for Methyldifluorophosphine[a]

	Ground state	$v_t = 1$ A level	$v_a = 1$	$v_b = 1$
A/MHz[b]	7155.34	7158.23	7168.00	7154.43
B/MHz	6815.25	6792.16	6818.97	6814.23
C/MHz	4364.54	4358.40	4340.26	4372.80
I_a/u Å^2 [c]	70.6292	70.6007	70.5045	70.6382
I_b/u Å^2	74.1537	74.4057	74.1133	74.1648
I_c/u Å^2	115.7914	115.9544	116.4392	115.5726
P_{aa}/u Å^2 [d]	59.6579	59.8797	60.0240	59.5496
P_{bb}/u Å^2	56.1334	56.0747	56.4152	56.0230
P_{cc}/u Å^2	14.4958	14.5260	14.0893	14.6152

[a] $V_3 = 2300 \pm 6$ cal/mol; $\theta = 25.0 \pm 0.4°$; $I_\alpha = 3.16$ u Å^2 (assumed). [b] Estimated uncertainties in rotational constants: ±0.05 MHz. [c] Rotational constant (MHz) = 505,376/(moment of inertia (u Å^2)). [d] $P_{aa} = {}^1/_2(I_b + I_c - I_a)$, etc.

Table III. The Stark Effect and Dipole Moments of Methyldifluorophosphine[a]

	$d\nu/dE^2$ [b]	
Transition	Obsd	Calcd
$0_{00}-1_{01}$	233.78	233.83
$1_{11}-2_{12}$	60.88	60.80
$1_{01}-2_{02}$	−73.38	−73.26
$1_{10}-2_{11}$	48.05	48.13

$\mu_a^2 = 4.191 \pm 0.010$ D^2 $\mu_a = 2.047 \pm 0.002$ D
$\mu_b^2 = 0.0$ D^2 (assumed) $\mu_c = 0.195 \pm 0.062$ D
$\mu_c^2 = 0.038 \pm 0.024$ D^2 $\mu = 2.056 \pm 0.006$ D

[a] $M = 0$. [b] Hz/(V/cm)^2. $\mu_{OCS} = 0.7152$ D assumed.

Table IV. Comparison of Dipole Moments of Some Phosphine and Difluorophosphine Derivatives

Compd	μ, D	Ref
Methylphosphine	1.100	8
Difluorophosphine	1.32	7
Cyanodifluorophosphine	2.393	5
Aminodifluorophosphine	3.029	3
Chlorodifluorophosphine	0.89	4
Methyldifluorophosphine	2.056	This study

Table V. Molecular Parameters of Some Difluorophosphine Derivatives

Compd	r(PF)	∠(FPF)	∠(FPX)	Ref
Methoxydifluorophosphine	1.586	95.3	101.5	6
Aminodifluorophosphine	1.586	94.7	101.7	3
Difluorophosphine	1.582	99.0	96.3	7
Chlorodifluorophosphine	1.571	97.3	99.2	4
Cyanodifluorophosphine	1.567	99.1	97.2	5

Table VI. PC Bond Length[a] and FPF and FPC Bond Angles[b] as a Function of the PF Bond Length[c]

r(PF)	r(PC)	∠(FPF)	∠(FPC)
1.576	1.838	98.9	97.4
1.578	1.834	98.8	97.5
1.580	1.829	98.6	97.6
1.582	1.825	98.4	97.8
1.584	1.820	98.3	97.9
1.586	1.816	98.1	97.9

[a] In angstroms. [b] In degrees. [c] Assumed: r(CH) = 1.093 Å; ∠(HCH) = 109.2°.

Table VII. Barriers to Internal Rotation in Methyldifluorophosphine and Related Compounds

Molecule	V_3/(cal/mol)	Tilt angle/deg	Ref
CH_3NH_2	1980	3.5	10
CH_3PH_2	1959	2.0	9
CH_3NF_2	4170	2.8	11
CH_3PF_2	2300		This study
CH_3AsF_2	1325	Not determd	12

bond length. Structural parameters for several PF_2X molecules are listed in Table V. A recent comparison[5] has demonstrated a significant correlation among PF bond length, FPF angle, and the electronegativity of the substituent attached to the PF_2 group. Using this correlation we expect the PF bond length in CH_3PF_2 to be near 1.582 Å. Table VI lists the values of the PC bond length and the FPF and FPC angles calculated from the experimental moments of inertia for six values of the PF distance near 1.582 Å.

From the data in Table VI we conclude that r(PC) = 1.82 (2) Å, ∠(FPF) = 98.4 (5)°, and ∠(FPC) = 97.8 (5)°.

Internal Rotation

The barrier to internal rotation, V_3, and the angle, θ, between the methyl group symmetry axis and the a principal axis of the molecule were determined to be 2300 (3) cal/mol and 25.0 (2)°, respectively, by least-squares fitting them to the observed A-E splitting in $v_t = 1$. For this calculation the moment of inertia of the methyl group was assumed to be 3.16 u Å^2 and the rotational constants used were those obtained from a rigid-rotor fit of the $v_t = 1$ A level transitions. The uncertainties given for V_3 and θ are standard deviations from the least-squares fit; they include no allowance for uncertainty in I_α. The angle θ has little correlation with I_α; however, V_3 does. This correlation may be expressed as $V_3 = 2300 - 620(I_\alpha - 3.16$ u Å$^2)$. The ground-state splittings were calculated with the same internal rotation parameters and the ground-state rotational constants.

According to the calculated structure the angle between the methyl group symmetry axis and the a principal axis is 25.3°, which may be compared with 25.0° obtained from the internal rotation analysis. The uncertainties in these two numbers are such that little can be deduced regarding the tilt of the methyl group. Table VII lists a selection of related molecules together with their barriers to internal rotation and their methyl group tilt angles. In each case the methyl group is observed to be tilted toward the lone pair on the group V atom. The trend in these tilt angles is for them to decrease both with substitution of fluorine for hydrogens on the group V atom and with increasing atomic number of this atom. Hence the fact that we have not observed a significant tilt is consistent with expectations.

Discussion

The comparison of barriers to internal rotation in CH_3PF_2 and related molecules in Table VII reveals two trends. First, the barrier in the series CH_3XF_2 decreases with increasing atomic number, and, second, replacing the fluorines with hydrogens lowers the barrier. However the increase in going from CH_3PH_2 to CH_3PF_2 is not as marked as from CH_3NH_2 to CH_3NF_2. This observation may be reconciled by using the argument given by Pierce, *et al.*,[10] to explain the high barrier in CH_3NF_2. They point out that the CNF angle in CH_3NF_2 is 7.4° smaller than the CNH angle in CH_3NH_2, and therefore increased barrier interactions in the fluorinated compound are expected. The CPH angle in CH_3PH_2, which is needed for a similar comparison in the phosphines, could not be determined in the electron diffraction study.[12] However, we have used the diffraction values for the methyl group parameters and the PH bond

(12) L. S. Bartell, *J. Chem. Phys.*, 32, 832 (1960).

length together with the moments of inertia from the microwave study[8] to derive a value for the CPH angle. The value obtained is dependent on several assumptions but it lies between 97.3 and 99.6° for all reasonable assumptions. From the present study the CPF angle is found to be 97.8°. Thus, although the CPF angle in CH_3PF_2 may be smaller than the CPH angle in CH_3PH_2, the difference is definitely less than the 7.4° difference found in the amines.

The dipole moment of CH_3PF_2 is 2.06 D; this is 0.74 D greater than the dipole moment of HPF_2.[7] A similar effect is found when we compare the dipole moments of CH_3NF_2[10] (2.57 D) and HNF_2[13] (1.92 D).

After making several assumptions we have obtained a value for the PC bond length of 1.82 Å; this compares with a value of 1.858 Å in CH_3PH_2.[12] This shortening effect observed on introducing fluorine atoms is well known: the pH bond length in HPF_2 is 1.412 Å[7] compared to 1.421 Å in PH_3;[14] the CN bond length in CH_3NF_2 is 1.449 Å[10] compared to 1.474 Å in CH_3NH_2.[9]

Hence, with respect to structure, dipole moment, and barrier to internal rotation CH_3PF_2 behaves in just the manner expected from a consideration of related molecules.

Acknowledgment. We acknowledge with appreciation the gift of a sample of CH_3PF_2 from Dr. K. Cohn.

Registry No. CH_3PF_2, 753-59-3.

---

(13) D. R. Lide, *J. Chem. Phys.*, 38, 456 (1963).

(14) C. A. Burrus, A. Jache, and W. Gordy, *Phys. Rev.*, 95, 706 (1954).

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163

Synthesis and Properties of 1,2-(2,3-Naphtho)-*o*-carborane[1]

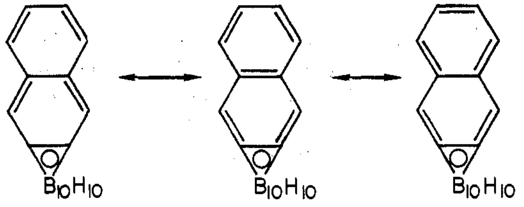
DONALD S. MATTESON* and ROGER A. DAVIS

Received August 16, 1973

Naphthocarborane has been synthesized, starting from dilithio-*o*-carborane and α,α′-dibromo-*o*-xylene, to form dihydronaphthocarborane, which on allylic bromination with *N*-bromosuccinimide yielded dibromodihydronaphthocarborane instead of the expected monobromo compound. Debromination with sodium iodide gave naphthocarborane, an air-sensitive, fluorescent yellow solid. Naphthocarborane readily adds bromine to the inner ring to form dibromodihydronaphthocarborane, oxygen to the inner ring to form a polymeric peroxide, and maleic anhydride or dimethyl acetylenedicarboxylate to the outer ring to form the corresponding Diels-Alder adduct. The proton nmr absorption of the outer ring of naphthocarborane appears at the same position as that of the ring protons of *p*-xylylene, which indicates that there is little if any effective π bonding between the cage and the ring system.

Introduction

Naphthocarborane[2] (**1**) (Figure 1) was chosen for study in the hope of answering some questions about the possible aromaticity of rings fused to carborane cages, which have only been partially answered by our studies of benzocarborane[3] and benzodicarbollide ion derivatives.[4] In the isomer chosen, the outer benzenoid ring can be fully aromatic only if the inner ring is also aromatic, with strong conjugation between the orbitals of the icosahedral cage and the π orbitals of the ring. Expressed in the terminology of resonance, structure **1** must be a polyene unless **2** and **3** contribute significantly to the resonance hybrid.



1 **2** **3**

The outer ring of naphthocarborane is far enough from the carborane cage so that some of the ambiguities in distinguishing electron delocalization effects from the steric and inductive effects of the cage encountered in the case of benzocarborane[3] might be resolved. It was also hoped that the extra delocalization energy to be gained by making a second ring aromatic might cause an increase in the ring-cage conjugation. However, it has turned out that naphthocarborane has some new ambiguities of its own, and the hope of proving that ring-cage conjugation is a significant structural feature has not been fulfilled.

Results

Synthesis. We expected that our synthesis of benzocarborane[3] would be readily adaptable to the preparation of naphthocarborane (**1**). It was, but not without some unexpected twists. The reaction of dilithio-*o*-carborane with α,α′-dibromo-*o*-xylene efficiently yielded 5,8-dihydronaphthocarborane (**4**).[5] However, bromination of **4** with *N*-bromosuccinimide did not yield the expected 5-bromo-5,8-

---

(1) (a) Preliminary communication by D. S. Matteson and R. A. Davis, *J. Chem. Soc. D*, 669 (1970); (b) supported by U. S. Public Health Service Research Grant No. CA-05513 from the National Cancer Institute; (c) abstracted from the Ph.D. Thesis of R. A. D., Washington State, University, 1971.

(2) A possible systematic name would be 1,2-(2,3-naphtho)-1,2-dicarba-*closo*-dodecaborane(12). By the system commonly in use for naming polycyclic compounds, possible names are naphtho-[2,3-*a*]-1,2-dicarba-*closo*-dodecaborane(12) or, in a system which would avoid any ambiguity in lettering higher numbered edges of the icosahedron, 1,2-dicarba-*closo*-dodecaborano(12)[1,2-*b*]naphthalene. There is, of course, another possible isomer, 1,2-(1,2-naphtho)-1,2-dicarba-*closo*-dodecaborane(12), but it would shed no light on the question of aromaticity raised here since it would have an aromatic benzene ring regardless of ring-cage interaction.

(3) (a) N. K. Hota and D. S. Matteson, *J. Amer. Chem. Soc.*, 90, 3570 (1968); (b) D. S. Matteson and N. K. Hota, *ibid.*, 93, 2893 (1971).

(4) D. S. Matteson and R. E. Grunzinger, Jr., *Inorg. Chem.*, 13, 671 (1974).

(5) We have arbitrarily numbered the rings of naphthocarborane like naphthalene, starting with 1, 2, 3, 4 for the CH groups of the outer ring and 5, 8 for those of the inner ring.