gas thermometer was evacuated, filled with helium gas and recalibrated.

Smoothed values of C_p are given in Table I. A plot of C_p/T *versus* T^2 is presented (Fig. 1). Such a plot is, of course, linear over the region in which the T^3 law is obeyed.

TABLE I

HEAT CAPACITY OF ORDERED Mg_3Cd AT ROUNDED TEMPERATURES

T, °K.	C_p, joules/ °K. g. atom	T, °K.	C_p, joules/ °K. g. atom
4	0.008	9	0.0829
5	.0145	10	.021
6	.0237	12	.239
7	.0370	14	.421
8	.0560	16	.638

The pronounced curvature in the plot in Fig. 1 makes the electronic specific heat coefficient as determined from the intercept somewhat uncertain. A provisional value of 0.8×10^{-3} joule/mole deg.² is obtained from the present data. This may be compared with 1.32×10^{-3} and 0.6×10^{-3} which have been obtained for magnesium[5] and cadmium,[6] respectively.

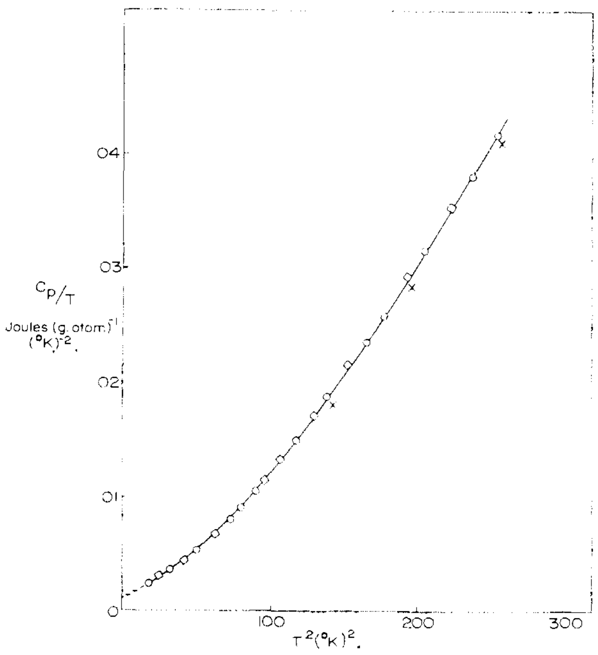

Fig. 1.—Heat capacities of ordered Mg_3Cd: This study, ○, 1st series; □, 2nd series; × data from ref. 4.

As is customary in work of this nature the effective Debye temperature θ is calculated from the experimental results. With help of data from reference 2 it is found that the Debye θ has a minimum of 226°K. at a temperature of 18°K. and approaches 292°K. at absolute zero. The curve of θ *versus* T is very similar to the same curve for Cd given by Smith and Wolcott. They have observed that both zinc and cadmium show a pronounced minimum in the θ-curve whereas magnesium does not. They have suggested that the minimum may originate with the same factors that produce the anomalous axial ratio in zinc and cadmium. It is of interest to note that Mg_3Cd also exhibits the minimum, despite the fact that it has a normal axial ratio.[7,8]

The authors wish to acknowledge the assistance of Mr. Kay F. Sterrett and Mr. Guido Galli in making the measurements contained in this communication.

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(5) P. L. Smith, *Phil. Mag.*, [7] **46**, 744 (1955).

(6) P. L. Smith and N. M. Wolcott, *ibid.*, 1 [8] 854 (1956).

(7) D. A. Edwards, W. E. Wallace and R. S. Craig, THIS JOURNAL, **74**, 5256 (1952).

(8) W. E. Wallace, *J. Chem. Phys.*, **23**, 2281 (1955).

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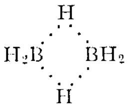
RECEIVED DECEMBER 22, 1956

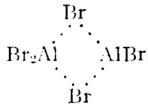
SINGLY-BRIDGED COMPOUNDS OF THE BORON HALIDES AND BORON HYDRIDES

Sir:

The existence of dimeric molecules in the hydride of boron, $(BH_3)_2$, the halides of aluminum and gallium, $(AlBr_3)_2$ and $(GaCl_3)_2$, and in the alkyls of aluminum, $(AlMe_3)_2$, has long provided a difficult hurdle for valency theory.[1] It is now accepted that these dimeric molecules involve doubly-bridged structures (I–III).



I



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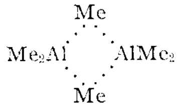
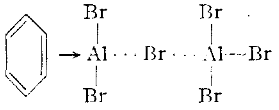


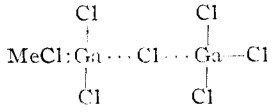
III

The precise interpretation of the electronic bonding in these bridged structures has been the subject of numerous discussion.[2]

Aluminum bromide reacts with aromatic hydrocarbons to form molecular species with the composition $ArH{\cdot}Al_2Br_6$ and $ArH{\cdot}AlBr_3$.[3] Likewise methyl chloride forms addition compounds with gallium chloride, $MeCl{:}Ga_2Cl_6$ and $MeCl{:}GaCl_3$.[4] The species $ArH{\cdot}Al_2Br_5$ and $MeCl{\cdot}Ga_2Cl_6$ were interpreted[3,4] as involving a single halogen bridge (IV, V).



IV



$$\mathrm{MeCl{:}\overset{Cl}{\underset{Cl}{Ga}}\cdots Cl\cdots\overset{Cl}{\underset{Cl}{Ga}}-Cl}$$

V

The boron halides are monomeric and exhibit no tendency to form doubly-bridged dimers. However, we have observed that 1:1 addition compounds of the boron halides with triethylamine and with pyridine are capable of absorbing a second equivalent of boron halide at temperatures from −78 to 0° to form relatively unstable 1:2 addition compounds. The following products have been synthesized: $Et_3N{:}2BF_3$, $Et_3N{:}2BCl_3$, $Et_3N{:}2BBr_3$, $Py{:}2BF_3$, $Py{:}2BBr_3$. At −78° triethylamine

---

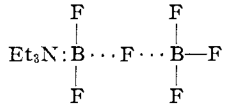
(1) See E. Cartmell and G. W. A. Fowles, "Valency and Molecular Structure," Academic Press, Inc., New York, N. Y., 1956, Chapter 13, for a summary and pertinent references.

(2) K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945); R. E. Rundle, *ibid.*, **69**, 1327, 2075 (1947); W. N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954).

(3) H. C. Brown and W. J. Wallace, THIS JOURNAL, **75**, 6265 (1953). Unpublished work with Dr. Sang Up Choi.

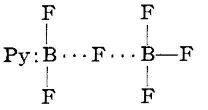
(4) H. C. Brown, L. P. Eddy and R. Wong, *ibid.*, **75**, 2675 (1953).

and 3-picoline in toluene solution absorb 2 molar equivalents of boron trifluoride. Consequently, in these cases the addition compounds exist in solution as well as in the pure phases. Although these compounds might be formulated as ion-pairs, $Et_3N:BF_2^+BF_4^-$ and $Py:BF_2^+BF_4^-$, their properties appear to be in better accord with the singly-bridged structures (VI, VII).



$$Et_3N:\underset{F}{\overset{F}{B}}\cdots F\cdots\underset{F}{\overset{F}{B}}—F$$

VI



$$Py:\underset{F}{\overset{F}{B}}\cdots F\cdots\underset{F}{\overset{F}{B}}—F$$

VII

An examination of the action of diborane on borane addition compounds at low temperatures has revealed similar higher order addition compounds. Thus, as shown by the vapor pressure data in Table I, pyridine–borane in diglyme solution absorbs a second molar equivalent of borane at 0° and a third at −64°: $Py:BH_3{\cdot}BH_3$ and $Py:BH_3{\cdot}B_2H_6$.

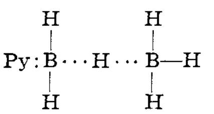
TABLE I

VAPOR PRESSURE–COMPOSITION DATA FOR DIBORANE AND PYRIDINE IN DIGLYME

0°		−64°	
Mole ratio B_2H_6/Py	Press., mm.	Mole ratio B_2H_6/Py	Press., mm.
0.51	2	1.15	2
.69	6	1.38	5
.79	8	1.51	7
.98	12	1.57	10
1.06	52	1.74	19
1.19	137	2.30	46
1.28	195	2.82	74

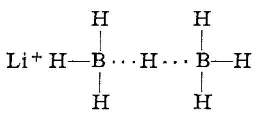
Similarly, triethylamine–borane adds a mole of borane at −64°, forming $Et_3N:BH_3{\cdot}BH_3$.

Finally, we have observed that both lithium and sodium borohydrides in diglyme solution absorb a molar equivalent of borane at 0°. Although the amine addition compounds might be formulated as borohydride ion-pairs $PyBH_2^+BH_4^-$, such a formulation is not possible for the corresponding derivatives of lithium and sodium borohydride. In view of the similarity of the phenomena under discussion, it appears preferable at this time to formulate these addition compounds in terms of single hydrogen bridges (VIII, IX).



$$Py:\underset{H}{\overset{H}{B}}\cdots H\cdots\underset{H}{\overset{H}{B}}—H$$

VIII



$$Li^+\ H—\underset{H}{\overset{H}{B}}\cdots H\cdots\underset{H}{\overset{H}{B}}—H$$

IX

The results suggest that numerous singly-bridged derivatives (without additional bonding) must exist in electron deficient systems and that electron valency theories proposed to account for the existence of doubly-bridged derivatives should, in all probability, also provide for the formation and existence of related singly-bridged structures.[5]

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RECEIVED FEBRUARY 6, 1957

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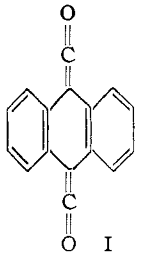
(5) It should be pointed out that the discussion by R. E. Rundle, *J. Chem. Phys.*, **17**, 671 (1949), strongly implies that singly-bridged derivatives of the type here reported should possess a measure of stability.

ANTHRAQUINOKETENE[1]

Sir:

Realization of an isolable, monomeric bisketene, anthraquinoketene (I), has been achieved by the dehydrochlorination of 9,10-dihydroanthracene-9,10-dicarbonyl chloride (IIa) using triethylamine. Except for the unique case of carbon suboxide this represents the first successful preparation of a bisketene. Although a substantial part of the extensive studies of ketenes has been concerned with their synthesis[2] the previous attempts to obtain a bisketene seem to have failed either because of the low reactivity of the starting material used or because of the rapid spontaneous polymerization of the product formed.[3]



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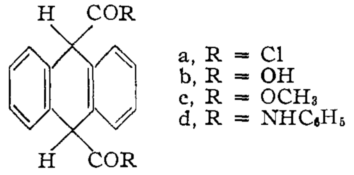

II

With all operations performed under an atmosphere of dry nitrogen, a benzene solution of IIa was permitted to react with triethylamine at room temperature for several hours, the quantitative precipitate of triethylamine hydrochloride filtered, and the red benzene filtrate concentrated. The bisketene I separated as orange-red crystals (needles) in *ca.* 90% yield. *Anal.* Calcd. for $C_{16}H_8O_2$: C, 82.75; H, 3.47. Found: C, 82.94; H, 3.52. Upon heating, I slowly transformed into a dark colored substance which is possibly polymeric. The thermal transformation appeared to be instantaneous at 150° but no m.p. was observed below 300°. In the infrared I showed strong absorption at 4.80 μ but no appreciable absorption in the carbonyl region (see Fig. 1). The ultra-

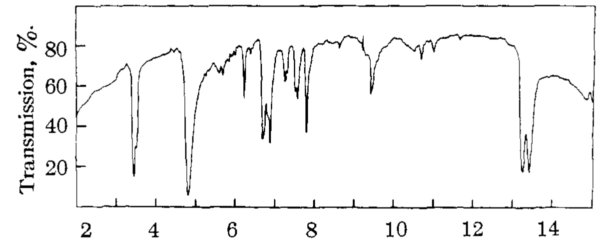

Fig. 1.—Infrared spectrum of anthraquinoketene, Nujol mull.

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(1) The work reported here was done as part of a general research program in organic chemistry at Cornell University sponsored by the B. F. Goodrich Company.

(2) W. E. Hanford and J. C. Sauer, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 109–140.

(3) H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, pp. 7–31.