L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovskii

1964

SovietRxiv

Abstract

Full Text

Chemistry

L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovskii

Some Features of the Structure and Reactivity of Barene Compounds

(Presented by Academician A. N. Nesmeyanov, February 14, 1964)

As we have shown earlier (1), barene compounds $B_{10}H_{10}C_2RR'$ (I) are formed in the reaction of decaborane with acetylene derivatives in the presence of substances that form complexes of the type $B_{10}H_{12}L_2$ with decaborane ($L = CH_3CN, (C_2H_5)_2S, (C_2H_5)_3As, HCON(CH_3)_2$, etc.):

$$B_{10}H_{14} + R'C \equiv CR' \xrightarrow{L} B_{10}H_{10}C_2RR'$$

I

A structure was proposed (2) for barene compounds in which two π-electrons of the carbon atoms of the barene nucleus, which are in a state close to sp^2-hybridization, participate in the formation of multicenter bonds with boron orbitals.

In the present work we report additional data on certain features of the structure of barene compounds, obtained on the basis of IR spectra* and from investigation of a number of chemical properties of this class of compounds. Figure 1 gives the IR spectra of barene, phenylbarene, vinylbarene, and two cyclic derivatives II and III. For comparison, the IR spectrum of decaborane is also given.

II III

In all IR spectra of barene compounds, the frequencies of stretching vibrations of bridging B—H—B bonds at 1580-1610 cm^{-1} are absent; from this it follows that the barene nucleus, in contrast to decaborane and the complexes $B_{10}H_{12}L_2$, contains no bridging hydrogens. For barene and its monosubstituted derivatives, the presence of a stretching-vibration frequency of the C—H bond of the barene nucleus at 3050-3075 cm^{-1} is characteristic, in a frequency region that overlaps with the region of stretching vibrations of the C—H bonds of the benzene ring. The presence of one strong absorption band in the region of C—H stretching vibrations in barene may serve as confirmation of the available chemical data on the equivalence of the carbon atoms in barene. In disubstituted barenes, the stretching-vibration frequencies of C—H bonds are absent from the IR spectra. It is interesting to note that, in contrast to barene, in the carboranes $B_3C_2H_5$ and $B_4C_2H_6$, according to Shapiro and co-workers (6) and Onak and co-workers (4), the IR spectra show no C—H stretching vibrations in the region 3000-3100 cm^{-1}. The frequencies of stretching vibrations of B—H bonds in barene appear as an unresolved multiplet in the region 2560-2640 cm^{-1}. Introduction of substituents causes splitting of the multiplet into separate lines. This confirms the available chemical data on the nonequivalence of the B—H bonds (and, correspondingly, of the boron atoms) in the barene nucleus. In the IR spectrum of B-decachlorobarene there are no frequencies characteristic of B—H bonds.

[Figure: IR absorption spectra. Horizontal scale: 400, 500, 600, 700, 1000, 1500, 2000, 2500, 3000 cm^{-1}. Vertical label: Absorption. Curves labeled $B_{10}H_{14}$, $B_{10}H_{10}$ derivatives, II, III.]

Fig. 1

In all IR spectra of barenes, as well as of decaborane, strong absorption is observed at 720—730 cm^{-1}; this frequency, apparently, may be assigned to stretching vibrations of B—B bonds (8). An important fact is the absence, in the IR spectra of all the barene compounds studied, of a frequency characteristic of an olefinic double bond, whereas in vinylbarene a strong line is observed at 1640 cm^{-1}. The absence of an ordinary double bond in barene also follows from chemical data (stability toward addition of halides, strong oxidants). In the spectrum of B-chlorobarene a new strong line appears at 890 cm^{-1}, which, as the number of chlorine atoms increases, is gradually shifted toward higher frequencies. In B-decachlorobarene all the indicated frequencies already appear in the form of a poorly resolved multiplet in the region 900-1050 cm^{-1}. Taking into account also the data of Cross(9), the line in the spectrum of B-chlorobarene at 890 cm^{-1} should be assigned to stretching vibrations of the B—Cl bond. In B-bromobarene, the strong line at 856 cm^{-1} apparently belongs to stretching vibrations of the B—B bond. In nitrobarene, obtained by the action of conc. nitric acid on barene, the strong line at 903 cm^{-1} evidently corresponds to stretching vibrations of $C—NO_2$.

Analysis of the IR spectra of carboxylic acids of the barene series shows that the stretching vibrations of the carbonyl group of barenecarboxylic acids occur in the region 1723-1731 cm^{-1}.

---

* We express our gratitude to N. Chumaevskii for providing the opportunity to record the IR spectra. The IR spectra of the barenes were recorded on a UR-10 instrument in the form of pressed pellets in KBr: in the interval 400-700 cm^{-1} with a KBr prism, in the interval 700-2800 cm^{-1} with a NaCl prism, and in the interval 2400-3500 cm^{-1} with a LiF prism.

Usually the frequencies of the stretching vibrations of the CO group in aliphatic carboxylic acids are located at 1700\$$\pm 5cm$^{-1}\$; however, the introduction of electron-acceptor substituents causes a shift of the CO-group frequency toward higher frequencies. Thus, for example, the absorption bands of the CO group for α-halocarboxylic acids are located at 1720–1740 cm^{-1}. These data confirm the proposition we expressed earlier that the barene nucleus is an electron-acceptor group (possesses an I-effect).

Investigation of the nuclear quadrupole resonance spectrum* for Cl^{35} of *p*-chlorophenylbarene, similarly to *p*-bromophenylbarene(5), shows that the barene nucleus, acting as a substituent in the benzene ring, is a group possessing a stronger I-effect than F, Cl, and COOH:

Frequencies of NQR of Cl^{35} at 77°K, MHz:

p-chlorophenylbarene	35.442	*p*-dichlorobenzene	34.736
p-fluorochlorobenzene	35.043	*p*-chlorobenzoic acid	34.673

The electron-acceptor effect of the barene nucleus is also manifested in the chemical properties of barene compounds.

cyclic formal of barenediol, V

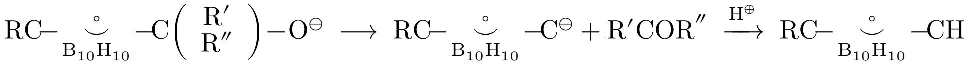
The presence of an I-effect can explain the fact of the unusual stability in an acidic medium of the cyclic formal V, which is not altered by many hours of boiling with 20% sulfuric acid**. Other examples in which the strong electron-acceptor effect of the barene nucleus is manifested may be the cases, found by two of us(10), of easy cleavage of the C—C bond in derivatives of barenecarboxylic and barenedicarboxylic acids under the action of basic reagents (C_2H_5ONa, $LiAlH_4$), with formation of barene.

Taking into account the strong electron-acceptor influence of the barene nucleus, we believe that in barene compounds capable of forming an anion of type VI, the C—C bond between the barene nucleus and the substituent should be readily cleaved, with intermediate formation of barenyl-anion:*

---

* We express our deep gratitude to G. K. Semin and V. I. Robas for the investigation of the NQR spectra of *p*-chlorophenylbarene, *p*-bromophenylbarene, chloromethylbarene, and di(chloromethyl)barene.

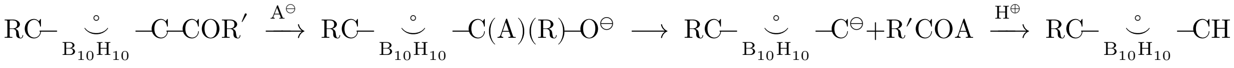
** A detailed description of the chemical transformations of barene compounds will be published in subsequent communications.



$$RC-\underset{B_{10}H_{10}}{\overset{\circ}{\smile}}-C\left(\begin{matrix}R'\\R''\end{matrix}\right)-O^{\ominus} \longrightarrow RC-\underset{B_{10}H_{10}}{\overset{\circ}{\smile}}-C^{\ominus} + R'COR'' \xrightarrow{H^{\oplus}} RC-\underset{B_{10}H_{10}}{\overset{\circ}{\smile}}-CH$$

VI

In particular, such compounds are those containing a carbonyl group bonded to the barene nucleus. In this case, the action of the corresponding nucleophilic reagent A can be represented as follows:



$$RC-\underset{B_{10}H_{10}}{\overset{\circ}{\smile}}-C-COR' \xrightarrow{A^{\ominus}} RC-\underset{B_{10}H_{10}}{\overset{\circ}{\smile}}-C(A)(R)-O^{\ominus} \longrightarrow RC-\underset{B_{10}H_{10}}{\overset{\circ}{\smile}}-C^{\ominus}+R'COA \xrightarrow{H^{\oplus}} RC-\underset{B_{10}H_{10}}{\overset{\circ}{\smile}}-CH$$

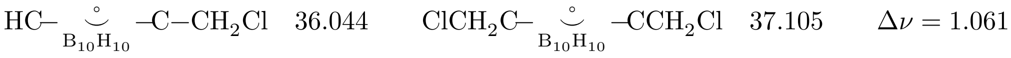
$$R' = H,\ Alk,\ Ar,\ OAlk,\ NR_2$$

The strong electron-acceptor effect (or electron deficiency) of the barene system accounts for the high proton mobility of hydrogen atoms bonded to carbon atoms ([11], [12]). Replacement of hydrogen atoms bonded to boron atoms by halogen atoms further increases this proton mobility, and B-decachlorobarene is a fairly strong acid ([13]).

Also characteristic of the barene system is the great lability of the electron cloud of the barene nucleus, which makes it easy for the influence of substituents to be transmitted through the nucleus. Thus, comparison of the Cl^{35} NMR spectra of chlorobenzene and *p*-dichlorobenzene* with the NMR spectra of chloromethylbarene and di(chloromethyl)barene shows that the difference between the frequencies of the dichloro derivative and the monochloro derivative in the benzene series is smaller than in the barene series, i.e., the influence of one chlorine atom on the other is manifested to a greater extent in the latter than in the former.

Cl^{35} NMR frequencies at −77°, MHz:

$$Cl-C_6H_5 \quad 34.622 \qquad p\text{-}Cl-C_6H_4-Cl \quad 34.779 \qquad \Delta\nu = 0.117;$$



$$HC-\underset{B_{10}H_{10}}{\overset{\circ}{\smile}}-C-CH_2Cl \quad 36.044 \qquad ClCH_2C-\underset{B_{10}H_{10}}{\overset{\circ}{\smile}}-CCH_2Cl \quad 37.105 \qquad \Delta\nu = 1.061$$

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
8 II 1964

CITED LITERATURE

1. L. I. Zakharkin, V. I. Stanko et al., *Izv. AN SSSR, ser. khim.*, 1963, 2238.
2. L. I. Zakharkin, V. I. Stanko et al., *Izv. AN SSSR, ser. khim.*, 1963, 2069.
3. R. Hoffman, W. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963).
4. T. Onak, R. Williams, H. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).
5. L. I. Zakharkin, V. I. Stanko et al., *DAN*, **155**, No. 5 (1964).
6. I. Shapiro, C. Good, R. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962); *J. Am. Chem. Soc.*, **85**, 3167 (1963).
7. H. Siebert, *Zs. anorg. u. allgem. Chem.*, **113**, 266 (1952).
8. W. Lehman, J. Shapiro, *Spectrochim. acta*, **17**, 396 (1961).
9. A. Cross, *Introduction to Practical IR Spectroscopy*, 1961, p. 105.
10. L. I. Zakharkin, Yu. A. Chapovskii, *Izv. AN SSSR, ser. khim.*, 1964, No. 4, 774.
11. L. I. Zakharkin, V. I. Stanko et al., *Izv. AN SSSR, ser. khim.*, 1963, 2236.
12. L. I. Zakharkin, V. I. Stanko, Yu. A. Chapovskii, *Izv. AN SSSR, ser. khim.*, 1964, No. 3, 582.
13. L. I. Zakharkin, V. I. Stanko, A. I. Klimova, *Izv. AN SSSR, ser. khim.*, 1964, No. 4, 771.

* Data of G. K. Semin and V. I. Robas.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.