SPECTRAL STUDY OF m-CARBORANEDICARBOXYLIC ACID AND THE PRODUCTS OF ITS SPLITTING AS MODELS FOR INVESTIGATING DECOMPOSITION OF CARBORANE-CONTAINING POLYAMIDES

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The structure of m-carboranedicarboxylic acid dianilide and the products of its degradation, which takes place with the formation of the corresponding dicarba-nido-undecaborate, was investigated by vibrational spectroscopy. The dianilide exists in two crystalline modifications: in one, the amide groups are bound by intermolecular H bonds of the NH...OC type, and they remain free in the other. The carborane nucleus in dianilide can be split into dicarba-undecaborate in softer conditions than with unsubstituted carborane. In the protonated form, the $H^+[Ph—NH—C(O)—C_2B_9H_{10}—C(O)—NH—Ph]^-$ proton, which reacts with the $—C(O)—C_2H_9H_{10}—C(O)—$ fragment, destabilizes the nido polyhedron. In prolonged standing in air or in heating, the protonated form decomposes with the formation of acetanilide and an amorphous residue containing products of deeper decomposition of nido-carborane, including boric acid.

Carborane-containing polyamides are efficient stabilizers of thermal and thermal oxidative decomposition of different classes of aromatic polymers [1]. The m-carborane nucleus contained in polyamides splits into the dicarba-nido-undecaborate anion when heated [2]. The dicarba-nido-undecaborate fragments formed in polyamides are the active origin of stabilization of different aromatic polymers [3]. Polyamides containing dicarba-nido-undecaborate fragments alone were subsequently obtained by nucleophilic splitting of the carborane nuclei in the polymer, and their properties were investigated in [4].

We synthesized 1,7-dicarba-closo-dodecaborane(12)-1,7-dicarboxyanilide (I), which models the elementary unit of poly-4,4'-diphenylene-1,7-carboranyldicarbamide [4], to study the "closo—nido" transition in carborane-containing polyamides. Compound (I) was the starting compound for preparation of 7,9-dicarba-nido-undecaborate(12)-7,9-dicarboxyanilide (III), which in turn models the elementary unit of the nido-carborane-containing polyamide.

The transformations of (I) were studied with the vibrational spectra. The Raman and IR spectra of (I) are shown in Fig. 1. The Raman spectrum was obtained for a crystalline sample, and the IR spectra were obtained for both crystalline samples and for a dilute solution in CCl_4. The spectra indicate the presence of a closo-carborane nucleus (νBH vibration with the center of gravity at 2610 cm^{-1} — the broad band in the IR spectrum of the solution, a complex multiplet in the IR spectrum of the crystal). The carborane icosahedron is an intense multiplet with the center at 775 cm^{-1} in the Raman spectrum. The —C(O)—NH— group is characterized by νNH bands in the ~3400 cm^{-1} region and νC=O bands in the 1700 cm^{-1} region and by bands of amide II (~1500 cm^{-1}) and amide III (~1200 cm^{-1}). The usual intense Raman lines at 1000, 1030, and 1600 cm^{-1} and νCH bands in the region of 3000-3100 cm^{-1} belong to a monosubstituted benzene ring. It is interesting that dianilide (I) is isolated as one of two crystalline modifications (Ia and Ib) as a function of the rate of crystallization. Modification (Ia) is formed in slow crystallization, and (Ib) is formed in fast crystallization. The spectra of (Ia) and (Ib) differ significantly (Figs. 2 and 3). In the spectrum of (Ia), the narrow νNH band has a frequency of 3420 cm^{-1} characteristic of free NH groups in secondary amides, and the νC=O band has a frequency of 1710 cm^{-1}. Almost the same bands are observed in the spectrum of a dilute solution of (I) in CCl_4. There is a doublet of νNH with reduced frequencies, 3365 and 3335 cm^{-1}, in the spectrum of (Ib), and

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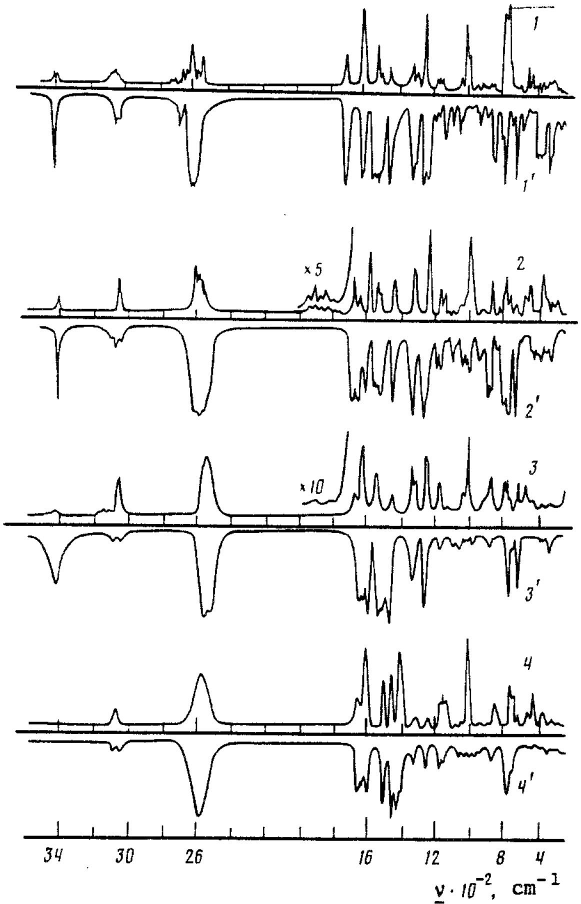


Fig. 1. Raman (1-4) and IR (1'-4') spectra of compound (I) (1, 1'), Cs salt (IIb) (2, 2'), protonated form (III) (3, 3'), and deuterated form (IIIa) (4, 4').

the νC=O frequency is also decreased to 1685 cm^{-1}. Dissolved in CCl_4, both modifications give the same spectrum. It follows that the amide groups in (Ib) are bound as usual by intermolecular hydrogen bonds of the NH...O=C type, while they remain free in (Ia). In Fig. 1 the spectra shown for substance (I) are of modification (Ia). Modifications (Ia) and (Ib) also differ in the low-frequency region of the Raman spectrum (Fig. 3), and this suggests that these substances have different crystal lattices. Note the presence of a broad, weak band at ~180 cm^{-1} in this region in (Ib), which apparently belongs to vibration of the NH...O=C hydrogen bond itself. There are cases in which substance (I) is separated in the form of a mixture of "free" (Ia) and "bound" (Ib) modifications in a different ratio during crystallization, and this can be judged by the IR spectrum (an example is given in Fig. 2, curve 4).

The m-carborane nucleus is degraded with the formation of anion (II), separated in the form of potassium salt (IIa) in this case, on treatment of (I) with alcohol base [4]. In addition, we showed that another nucleophile, Na hydride, can be used for splitting the closo-carborane nucleus in molecule (I). The corresponding cesium salt (IIb) was obtained with this method and subsequent treatment of the corresponding solution with Cs chloride. A comparison of spectra of (I) with the spectra of salts (II) reveals the same changes observed previously in studying the transition of the icosahedral closo-carborane into a nido-polyhedron [5-8]. The spectrum of cesium salt (IIb) is shown in Fig. 1. Note that the νBH band is shifted to the low-frequency region and its center of gravity is now located at 2550 cm^{-1}. Weak bands corresponding to vibration of "extra hydrogen" in the 2000-1750 cm^{-1} region can be found in the Raman spectrum, and in contrast to [6-8], no increase in the sensitivity of the pickup-recording circuit of the Raman spectrometer is required. It is interesting that the band corresponding to vibration of the "extra hydrogen" in the spectrum of salts (II), as in the spectrum of other m-carborane anions [6-8], has a complex structure, apparently due to Fermi resonance. The frequency of νC=O in the spectrum of salts (II) decreases to ~1670 cm^{-1}, since the C=O groups are now conjugated with the open face of the dicarbaundecaborate anion, in agreement with [9]. The νC=O band has the usual

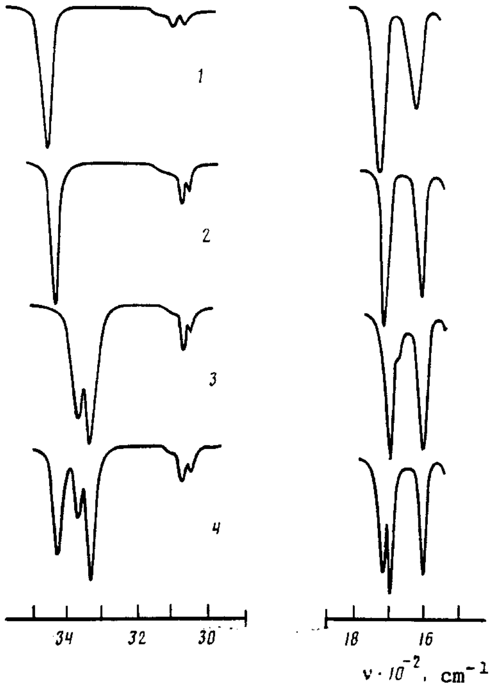


Fig. 2

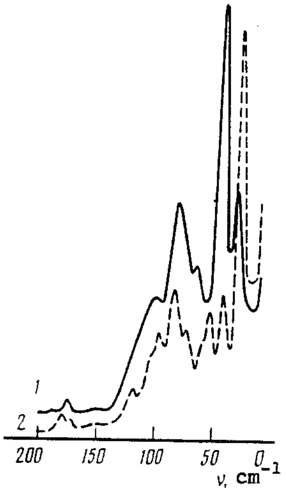


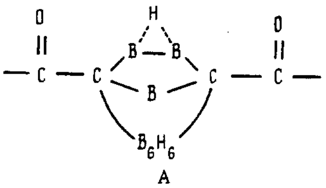
Fig. 3

Fig. 2. IR spectra of compound (I): 1) solution in CCl_4 (c = 0.01 mole/liter); 2, 3) crystalline modifications of compound (I): (Ia) (2), and (Ib) (3); 4) mixture of (Ia) and (Ib).

Fig. 3. Low-frequency region of the Raman spectrum of crystalline modifications of compound (I): 1) (Ia); 2) (Ib).

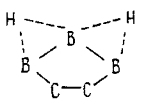
intensity for a conjugated amide group. The bands of amides II and amides III in the spectrum of salts (II) are also slightly shifted to the low-frequency region. The presence of a narrow band of νNH with a frequency of ~3410 cm^{-1} in the IR spectrum of solid samples of (II) indicates the absence of intermolecular hydrogen bonds.

The vibrational spectra thus clearly indicate the formation of the 7,9-dicarba-nido-undecaborate anion with an "extra hydrogen," which occupies the bridge position between two neighboring boron atoms on the open face:

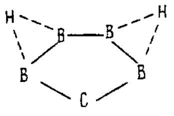


A

When salts (II) are treated with an aqueous solution of HCl or after they are passed through a column packed with a cation-exchange resin, the "acid" $H^+[Ph{-}NH{-}C(O){-}CB_9H_{10}C{-}C(O){-}NH{-}Ph]^-$ (III), an amorphous white powder unstable on prolonged storage in air, is easily formed. It was interesting to determine the position of the proton in the molecule of (III). In protonation of 7,8- and 2,7-dicarba-nido-undecaborates, the proton occupies the second free BHB bridge position between neighboring boron atoms on the open face:



B

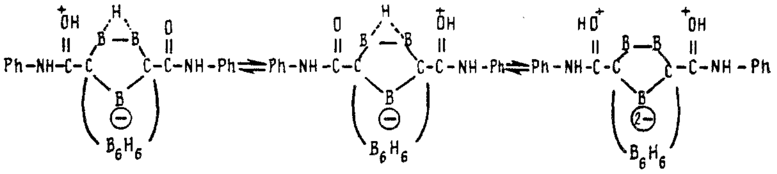


C

in the case of 7,8-(B) and in the case of 2,7-nido-anions (C) [7]. However, the molecule of (II) contains a 7,9-anion and the new BHB bridge on the open face cannot form a second proton. The spectrum of "acid" (III) (Fig. 1) differs from the spectra of salts (II). First, the lines in the spectrum are strongly broadened and there are no vibrations of the crystal lattice in the low-frequency region, which confirms the amorphism of the sample. The broad νBH band has the center of gravity at 2550 cm^{-1}, i.e., the nido structure of the polyhedron is preserved. The position of the νNH band also virtually does not change and the NH group is consequently not protonated. The basic changes are observed in the region of vibrations of the carbonyl group. The literature (for example the NMR data in [10]) also indicates that protonation of the carbonyl group basically takes place in the reaction of anilides with acids. Figure 1 shows that the frequency and intensity of νC=O decrease in both the Raman and in the IR spectrum. The vibrations of the extra hydrogen, which were adequately recorded in the Raman spectrum of (II), could not be observed in (III). As a consequence, the acid proton in (III) reacts in some way with the entire $-C(O)-CB_9H_{10}C-C(O)-$ fragment. Deuteration of both atoms of the extra hydrogens with the formation of compound (IIIa) was conducted to confirm the structure of compound (III). The band of νC=O in the spectrum of (IIIa) is shifted down by another 10 cm^{-1}; the structure of the spectrum is totally altered in the region below 1600 cm^{-1}, apparently due to a change in the shape of the vibrations, as in the case of deuteration of the extra hydrogens of other derivatives of dicarba-nido-undecaborane [7].

Deuteration of compound (III) thus confirms the reaction of the protons with the C=O groups and nido-carborane anion. In comparing the spectra of (III) and (IIIa), note that the band of νNH stretching vibrations disappears in the spectrum of (IIIa), which also indicates deuteration of the amide proton, but the νND band cannot be observed, since the broad intense νBH band is superimposed on it. The νND band actually appears as a shoulder with a frequency of 2560 cm^{-1} in deuteration of the amide proton in compound (I), where the closo-BH bond produces a band at 2600 cm^{-1} in the IR spectrum.

We will hypothesize that a fast exchange process caused by tunneling of the extra hydrogen and acid "extra-extra" hydrogen takes place in compound (III).



The equilibrium is apparently shifted toward protonation of both carbonyl groups. The involvement of the bridge extra hydrogen in this process causes the formation of a doubly charged dicarbolide anion in the molecule of the zwitterion type.

Crystalline needles of a new substance whose spectrum totally coincides with the spectrum of acetanilide grow inside the amorphous powder on prolonged standing of the protonated form of (III) in air (for several months). This means that the C—B bonds in the dicarba-nido-undecaborate fragment break and the carbon atoms of the open face pass into the organic part of the molecule under the effect of the oxygen and moisture in the air. Judging by the IR spectra, residues of the carborane nucleus are partially oxidized into boric acid. Acetanilide is also identified in the mixture with the NMR spectra [11]. The intense decomposition of compound (III) which we observed after 2 h of heating in a vacuum at 130°C, was also accompanied by distillation of acetanilide. The instability of compound (III) in comparison to salt forms (II) has not yet been explained and will be the subject of a subsequent study.

It was previously hypothesized in [3] that protonated undecaborate fragments, whose products of decomposition undergo oxidative processes in the stabilized polymers in the testing conditions in [2], are the active origin of stabilization in thermal oxidative decomposition of polymeric composites containing polycarboranylene amide as a stabilizer. The stabilizing effect of compounds containing mobile hydrogen (amines and phenols) is well known. Our results concerning the instability of the protonated form (III) in comparison to the salt form (II) can be useful in establishing the mechanism of the stabilizing effect of polycarbonylene amides in thermal oxidative decomposition of polyheteroarylenes and their composites.

EXPERIMENTAL

The Raman spectra of the solid samples were obtained in the 5-4000 cm^{-1} region on a Jobine–Ivonne HG-2S Raman laser spectrometer with excitation of the 5145 Å line of an ILA-2 argon laser with a power of ~200 mW. The IR spectra of both solid samples and solutions in CCl_4 were obtained on a UR-20 spectrophotometer in the 400-4000 cm^{-1} region.

Preparation of $[PhN(H)C(O)CB_9H_{10}CC(O)N(H)Ph]^-Cs^+$ (IIb). Here 0.16 g (67 mmoles) of NaH was sprinkled in a solution of 1 g (27 mmoles) of (I) in 10 ml of THF and stirred for 2 h in an Ar current at 5°C until liberation of H_2 stopped. The unreacted NaH was filtered off, 15 ml of H_2O was added to the solution, and the THF was evaporated in a water-jet pump vacuum at 30°C. After filtration, unreacted (I) in the amount of 0.1 g (10%) was separated, and a calculated amount of CsCl was added to the aqueous solution. The precipitated sediment was filtered and vacuum dried at 64°C, yield 38.79%. Found, %: C 37.68, H 4.40, B 18.93, N 5.44. $C_{16}H_{22}O_2B_9N_2Cs$. Calculated, %: C 8.10, H 4.36, B 19.29, N 5.59.

Preparation of $[PhN(H)C(O)CB_9H_{10}CC(O)N(H)Ph]^-H^+$ (III). Compound (III) was prepared by protonation of salt (II) in a column packed with Dowex 50W × 10 cation-exchange resin (20-50 mesh) [4]. Analogous results were obtained in protonation of anion (II), obtained by splitting the carborane nucleus in molecule (I) with Na hydride in THF. Compound (III) was lyophilically dried at a low temperature in a vacuum. The solid white residue formed was dried to a constant weight in a vacuum desiccator at ~20°C over P_2O_5. The yield of (III) was 0.7 g (85%). T_m = 140-150°C (with decomposition). Found, %: C 51.42, H 6.57, B 25.48, N 7.89. $C_{16}H_{23}O_2B_9N_2$. Calculated, %: C 51.24, H 6.68, B 26.01, N 7.49. When samples of compound (III) were stored in air in a closed box at ~20°C for 4 months, needle-shaped crystals formed on the surface of the sample, accompanied by caking of the basic substance in a viscous, amorphous mass. The IR and Raman spectra of these crystals were totally identical to the spectra of acetanilide. Significant amounts of boric acid were present in the amorphous mass.

Deuteration of Compound (I). Here 1 ml of DCl (30% solution in D_2O) was added to a solution of 0.38 g (10 mmoles) of $PhN(H)C(O)CB_{10}H_{10}CC(O)N(H)Ph$ in 2 ml of CD_3OD and the suspension formed was stirred in a magnetic stirrer for 1 h at ~20°C; 5 ml of D_2O was then added, and CD_3OD was evaporated at ~20°C and reduced pressure. The precipitated residue was washed with D_2O to neutral medium and dried to a constant weight. Yield 0.35 g (94%).

Preparation of $[PhN(D)C(O)CB_9H_9DCC(O)N(D)Ph]^-D^+$ (IIIa). A solution of acid (III) in D_2O was treated with cation-exchange resin in the D^+ form for 0.5 h at ~20°C, the solution was lyophilically evaporated, and compound (IIIa) obtained was dried at 30°C over P_2O_5 to a constant weight.

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