Letters to the Editor

Lengthening of O—H distance of the intramolecular O—H...O hydrogen bonds in molecular systems with conjugation

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Recently[1] on the basis of neutron diffraction data a dependence of the distances $d_{\mathrm{O-H}}$ and $d_{\mathrm{O...H}}$ within the hydrogen bond (HB) O—H...O on the distance $d_{\mathrm{O...O}}$ was obtained. Previously,[2—4] for several H-bonded systems, *e.g.*, enolic forms of β-diketones, a concept of synergism of HB and conjugation has been developed. It was called a "resonance-assisted hydrogen bond" (RAHB).[4] A comparison of the above-mentioned dependence with the appropriate data for RAHB containing systems is lacking in the literature. This work fills in that gap.

The dependence for the common H-bonded systems[1] and data obtained from the literature[4—8] for systems with RAHB are shown in Fig. 1. Their juxtaposition allows one to detect a number of distinctions of RAHB containing systems. First, in the distance $d_{\mathrm{O...O}}$ range of 2.55—2.62 Å the bond lengths $d_{\mathrm{O-H}}$ are almost the same for both systems but distances O...H are noticeably longer in the case of the RAHB containing systems. Second, in the distance $d_{\mathrm{O...O}}$ range of 2.40—2.50 Å the dependence obtained by us more rapidly deviates from the O—H branch toward the O...H branch. This points to the abnormal (relative to common systems) lengthening of the O—H bond in the same range of $d_{\mathrm{O...O}}$. Third, the deflection point of the dependence (obtained by interpolation) corresponds to greater O—H and O...H distances (~1.27 Å *vs.* 1.20 Å) and lesser O...O distances (region within 2.40—2.49 Å *vs.* 2.39 Å). The observed scattering of points at small $d_{\mathrm{O...O}}$ values is probably caused by the fact that the character of the potential energy surface (PES) of RAHB is dependent not only on $d_{\mathrm{O...O}}$ distance but also on other factors.

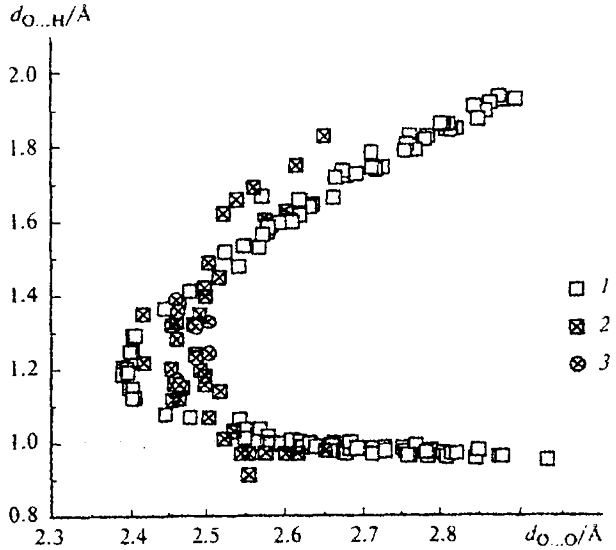

Fig. 1. Juxtaposition of the internuclear distances $d_{\mathrm{O...H}}$ and $d_{\mathrm{O...O}}$ obtained by neutron diffraction for common molecular systems[1] (*1*), by X-ray diffraction for systems with conjugation[4—7] (*2*), and by neutron diffraction for systems with conjugation[4,5,7,8] (*3*).

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e.g., electron-vibrational interaction.[9] Moreover, since the RAHB containing systems in solution are characterized with a double well PES with a small barrier,[5] the packing density may as well influence the PES form in the crystal.

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Separation of racemic *closo*-3,3-($\eta^{3,2}$-norbornadienyl)rhodacarboranes into enantiomers by HPLC on chiral stationary phases

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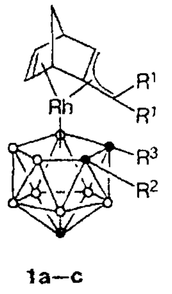
Racemic *closo*-rhodacarboranes, *viz.*, *closo*-3,3-($\eta^{3,2}$-C_7H_7-2-CR^1_2)-1-R^2-2-R^3-3,1,2-$RhC_2B_9H_9$ ($R^1 = R^2 = R^3 = H$; $R^1 = H$, $R^2 = R^3 = Me$; $R^1 = R^2 = R^3 = Me$) and *closo*-2,2-($\eta^{3,2}$-C_7H_7-2-CH_2)-2,1,7-$RhC_2B_9H_{11}$), were successfully separated into enantiomers by high-performance liquid chromatography (HPLC).

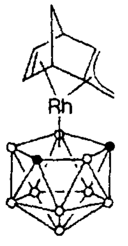
Key words: *closo*-rhodacarboranes, high-performance liquid chromatography, enantiomers, chiroptical properties.

High-performance liquid chromatography (HPLC) on chiral sorbents is one of the most convenient methods for the analysis of enantiomers and practical preparation of optically active π-complexes. This method has opened up new opportunities of obtaining high-purity enantiomers even from racemates that have no suitable functional groups for the synthesis of diastereomers and their subsequent separation by classical crystallization methods.[1,2] Only recently, HPLC has become the object of extensive use for the preparation of chiral metallacarboranes, which, however, are mostly sandwich bis(dicarbollyl)[3] and π-cyclopentadienyl-π-dicarbollyl[3,4] complexes with functional groups in the carborane ligand.

Using HPLC on chiral phases, we could separate for the first time a series of semisandwich *closo*-rhodacarboranes (*closo*-3,3-($\eta^{3,2}$-C_7H_7-2-CR^1_2)-1-R^2-2-R^3-3,1,2-$RhC_2B_9H_9$ (**1a—c**) and *closo*-2,2-($\eta^{3,2}$-C_7H_7-2-CH_2)-2,1,7-$RhC_2B_9H_{11}$ (**2**)) into enantiomers.



1a—c



2

	a	b	c
R^1	H	H	Me
R^2	H	Me	Me
R^3	H	Me	Me

Racemic complexes **1a** and **2**, which are known to be highly efficient catalysts for the diastereoselective hydrogenation of metacycline,[5,6] could be separated on

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