[CONTRIBUTION FROM THE INSTITUTE DI CHIMICA FISICA DELL'UNIVERSITÀ DI FIRENZA, FLORENCE, ITALY]

The Resolution of Complex Antipodes by Optically Active Solids[1]

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Following the work of John C. Bailar, Jr., and others on the resolution of antipodes of tetrahedral and octahedral complexes by means of adsorption of one isomer on optically active quartz powder, the authors extended the investigation to other optically active solids, with particular reference to the resolution of bis-(benzoylacetonato)-Be(II) in benzene through preferential adsorption on both *dextro* and *levo* sodium chlorate crystals.

Discussion

Several authors have studied the partial resolution of optically active chelate compounds by means of the preferential adsorption of the antipodes on either optically active quartz or particular hexoses. Henderson and Rule,[2] for example, obtained a partial resolution of the antipodes of *para*-phenylene-bis-iminocamphor by preferential adsorption in a column containing *d*-lactose. More recently, Moeller and Gulyas[3] obtained a partial resolution of the antipodes of the tri-(acetylacetonato) complexes of chromium(III) and cobalt(III) by the techniques and adsorbers used by Karagunis and Coumoulos.[4] Their experiences showed the antagonistic behavior between the nature of the adsorber and that of the adsorbed antipode (*i.e.*, *dextro* quartz preferentially adsorbs the *levo* antipodes).

Tsuchida, Kobayashi and Nakamura[5] partially resolved chloro-bis-(dimethylglyoximino)-ammine-cobalt(III) by this method although the magnitude of the specific rotation obtained varied with the concentration of the solution and the previous history of the powdered quartz.

Bailar[6] and co-workers subsequently successfully used this method in the partial resolution of several chelate compounds, including bis-(benzoylacetonato)-beryllium(II), for which the demonstration of optical activity provides evidence for tetrahedral coördination to beryllium(II).

The object of this work was to determine whether the preferential adsorption shown by quartz is a specific property or whether it is also demonstrated by non-centrosymmetric ionic crystals. The adsorption of bis-(benzoylacetonato)-beryllium(II) on one form of powdered sodium chlorate was studied. Sodium chlorate was chosen because it is an ionic compound of known morphological and structural properties which can be obtained easily in large crystals of high purity. The enantiomorphic forms of these crystals can be separated through polarimetric examination. In addition, their habit can be modified by crystallization from solution containing particular added substances.[7]

Large crystals of *dextro*- and *levo*-sodium chlorate were formed by crystallization from slightly supersaturated, carefully filtered solutions over a period of several days by slow cooling and slow evaporation. The crystals were large enough (several grams) and transparent enough for polarimetric examination to allow the detection and separation of twins.

Experimental

Bis-(benzoylacetonato)-beryllium(II) was prepared according to the method of Booth and Pierce.[8] The technique used in the resolution is that described by Bailar and Busch,[6] except that quartz has been replaced by carefully ground and dried sodium chlorate crystals.

Because of small observed optical rotations of the compound in the sodium D-line region, a special polarimetric apparatus[9] was employed which allowed use of the near violet region. Because of the low rotations (less than one degree) it was possible to obtain readings of remarkable accuracy with this instrument. For the rotational amplitudes, the errors due to the optical and mechanical adjustments of the polarimeter were negligible for the 0.002° precision required in the measurements. Therefore, great care was used in the stabilization of the photomultiplier electronics (less than 0.05%) and the light source. The latter was a tungsten-ribbon lamp which is cooled uniformly by a thermostated air stream of constant speed (1 m.^{3}/hr. ± 1%).

The polarimetric cells were 46 cm. long (the maximum length permitted by the optical path of the instrument) and were fitted with fixed windows in order to avoid errors due to non-reproducible strain produced by window-fastening devices. Because of the high index of refraction of the benzene solutions, great care was exercised in maintaining uniform temperature in the cells. The room containing the instrument was maintained at constant temperature (± 1°) and the jacketed cell had water from a large tank in the room flowing through it at a constant speed of 10 ml./min. The temperature in the cell was thus able to be maintained between ±0.001° during the measurements.

The samples were filtered at least twice through a double Jena G. 4 filter in an atmosphere of benzene vapor in order to avoid concentration changes of the benzene solutions. Under these conditions the polarimetric measurements were reproducible within 1–2%. The zero position of the polarimeter was determined with solutions of racemic bis-(benzoylacetonato)-beryllium(II) or with benzene samples treated with sodium chlorate, both solutions being filtered as described above.

The polarimetric measures were made by the method of symmetric angles. Fifteen pairs of readings were performed on each sample using different symmetrical angles. For ten of these pairs a photometric sensibility was used which was half that of the maximum sensibility (which was used for the remaining five pairs of readings).

The concentration of the solutions was 1.8% and the wave length of the radiation was 4360 ± 5 Å. The figures given below are average observed optical rotations of the solutions obtained from four series of different adsorber samples (see table).

The racemization times agree completely with those given by Bailar and Busch.[6]

Conclusions

Since the *levo* sodium chlorate shows a feeble preferential adsorption, the positive effect shown

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(1) Presented in part before the International Conference on Coördination Chemistry, London, England, April 6–11, 1959.

(2) G. M. Henderson and H. G. Rule, *Nature*, **141**, 917 (1938).

(3) T. Moeller and E. Gulyas, *J. Inorg. & Nuclear Chem.*, **5**, 245 (1958).

(4) G. Karagunis and G. Coumoulos, *Nature*, **142**, 162 (1938).

(5) R. Tsuchida, M. Kobayashi and A. Nakamura, *J. Chem. Soc. Japan*, **56**, 1339 (1935); *Bull. Chem. Soc. Japan*, **11**, 38 (1936).

(6) J. C. Bailar, Jr., and D. H. Busch, THIS JOURNAL, **76**, 5352 (1954).

(7) H. E. Buckley, "Crystal Growth," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 555.

(8) H. S. Booth and D. G. Pierce, *J. Phys. Chem.*, **37**, 59 (1933).

(9) R. Cini, *La Ricerca Scientifica*, in press.

Adsorber	Support	Obsd. rotation
$NaClO_3$	D	+0.067 ± 0.003°
$NaClO_3$	L	0
$NaClO_3$	Merck	+0.071 ± 0.003°
$NaClO_3$	50%D–50%L	+0.017 ± 0.002°

by Merck $NaClO_3$ must be due primarily to the *dextro* form in this mixture of the antipodes. It must be emphasized that this is due to the fact that the preferential adsorption is not equal for both antipodes, a phenomenon which has been noticed by other authors for adsorbers which differ both in chemical constitution and (if minerals) locality of occurrence. This indicates that the adsorption mechanism, even if extensible to ionic compounds, must be quite complex.

These results indicate that preferential adsorption on optically active solids is a general phenomenon, since several other authors have also carried out similar separations of substances which are different in chemical constitution and bond type.

Apart from these general theoretical considerations, this work indicates that it may be possible to use sodium chlorate for other investigations in preferential adsorption, because the substance may be usable without separation of the antipodes as a result of unequal preferential adsorption by them.

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The Dipole Moments and the Structure of Borazole and its Derivatives

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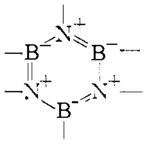
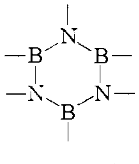
The dielectric constants and densities of dilute solutions of borazole, B-trichloroborazole, B-trichloro-N-trimethylborazole, hexamethylborazole, B-triethyl-N-trimethylborazole, hexaethylborazole, B-trimethyl-N-triphenylborazole and B-triethyl-N-triphenylborazole in benzene have been measured and used to calculate the dipole moments of the molecules. The values of the moments are considerably great for this kind of molecules apparently having a symmetric structure. A possible explanation is afforded first by the deviation from the coplanar structure and secondly by the excitation of molecular vibrations leading to temporary polar structures of the molecules. The possibilities of these alternatives are discussed for various substituted borazoles.

Introduction

A perfectly coplanar structure for certain substituted benzenes has for some time been disputed by some authors. Bastiansen and Hassel[2] in their study of a number of chloro- and bromobenzenes found that with the exception of *p*-dibromobenzene with its bromine atoms far apart, all models representing plane molecules gave sets of interatomic distances in poor agreement with the values obtained from electron diffraction experiments. These investigators tried models in which carbon–halogen bonds were bent out of the plane of the C_6-hexagon and showed that under these circumstances a better agreement between calculated and observed distances could be reached.

Borazole is isoelectronic with benzene. However, since nitrogen is more electronegative than boron, electrons are presumed to be denser around nitrogen atoms than around boron atoms, thus are not distributed uniformly over the six atoms of the ring as in the benzene molecule. The structure may be represented by an intermediate state between the two electronic states





For this reason, the deviation from the coplanar structure, if it exists at all, is presumed to be more pronounced in borazole derivatives than in substituted benzenes.

The dipole moment of borazole has been determined by Ramaswamy[3] as 0.67 D. in the gaseous state. Owing to the lack of sufficient stability of this compound, the author himself does not place much reliance on his data and suggests that further confirmation is required. Some of the derivatives of borazole are more stable than their mother compound and yet no data are found in the literature on the dipole moments of any of these derivatives. The present investigation has been undertaken in an effort to bring to light possible deviations from the coplanar structure by measuring the dipole moments of borazole and some of its drivatives.

Materials

Borazole was prepared by the reduction of B-trichloroborazole described below. The method was essentially the same as that proposed by Schaeffer, *et al.*,[4] differing in that $NaBH_4$ was used in place of $LiBH_4$ and that triethylene glycol dimethyl ether rather than dibutyl ether was employed as a solvent. Triethylene glycol dimethyl ether having a boiling point quite different from that of borazole was more suitable than diethylene glycol dimethyl ether.[5] Sodium borohydride (23.5 g.) was dissolved in 120 cc. of triethylene glycol dimethyl ether in an atmosphere of dry nitrogen. B-Trichloroborazole (30 g.) suspended in 75 cc. of the same solvent was gradually added to it at room temperature. Stirring was continued for about 2 hr. After the reaction was over, the product was distilled under reduced pressure and was collected in a trap cooled with Dry Ice. The yield of crude borazole was about 10 g. Vacuum distillation was repeated five times immediately before physical measurements.

B-Trichloroborazole and B-trichloro-N-trimethylborazole were prepared by essentially the same method as de-

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[1] Shionogi Pharmaceutical Co. Ltd., Amagasaki, Japan.

[2] O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, **1**, 489 (1947).

[3] K. L. Ramaswamy, *Proc. Indian Acad. Sci.*, **A2**, 364, 630 (1935).

[4] R. Schaeffer, M. Steindler, L. Hohnstedt, H. S. Smith, Jr., L. B. Eddy and H. I. Schlesinger, THIS JOURNAL, **76**, 3303 (1954).

[5] The use of this solvent was suggested by G. W. Schaeffer, private communication.