Polymorphic Behavior and Melting Points of Certain Benzocrown Ether Compounds

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Freshly prepared samples of dibenzo-24-crown-8 and 4-*t*-butylbenzo-15-crown-5 were found to have melting points which varied significantly from those origionally reported in the scientific literature. Samples prepared for the origional report were obtained, and were compared with the new samples. The origional report was found to be in error and the corrected values are provided. Dibenzo-24-crown-8 was found to exist as at least three polymorphs. One of these is a glass. The other two are crystalline, but have identical melting points. It was discovered that the less stable form is thermally converted to the more stable form at temperatures below its melting point.

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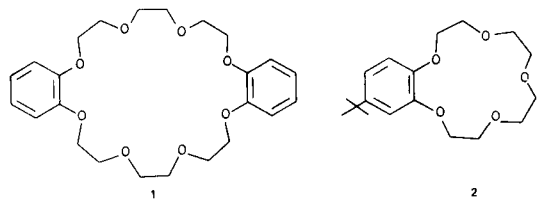
Introduction.

The class of compounds known as crown ethers was first reported in 1967 (1). They might best be defined as cyclic oligomers of ethylene oxide. As would be expected, such compounds exhibit peculiar behavior, most noticeable of which is their ability to form stable complexes with alkali metal cations. For this reason crown ethers have been studied extensively with regard to their ability to catalyze reactions of inorganic salts in organic media, and to selectively extract various ions into organic media (2).

Some degree of disparity has surrounded the physical constants of two of these compounds: dibenzo-24-crown-8 (1), and 4-*t*-butylbenzo-15-crown-5 (2).

Figure 1



1 2

Melting Points.

The melting point origionally reported for dibenzo-24-crown-8 is 113-114° (1). Other researchers have been unable to duplicate this value, and most report values between 101 and 104° (3-6). In the same initial report, 4-*t*-butylbenzo-15-crown-5 was reported to have a melting point of 43.5-44.5°. This material prepared in our laboratory, but by the same method, had a melting point of 96-98°. To clarify matters concerning these melting points, samples of the materials prepared for the initial report were obtained (7).

Comparison of the melting point of the origional sample of dibenzo-24-crown-8 with our product showed the origional report to be in error by 10°, as the origional sample actually melts from 103-104°, and has an infrared spectrum identical to that of polymorph-α of our product

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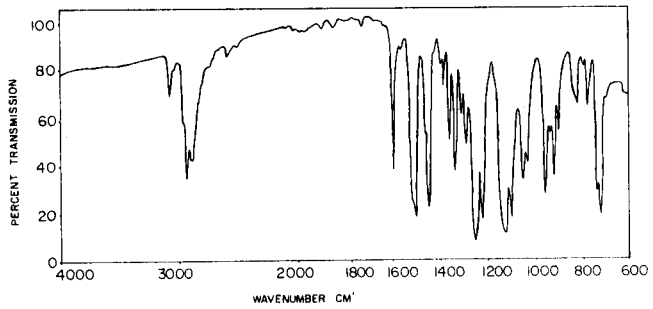

Figure 2. Infrared Spectrum of Dibenzo-24-crown-8, polymorph-α (potassium bromide pellet).

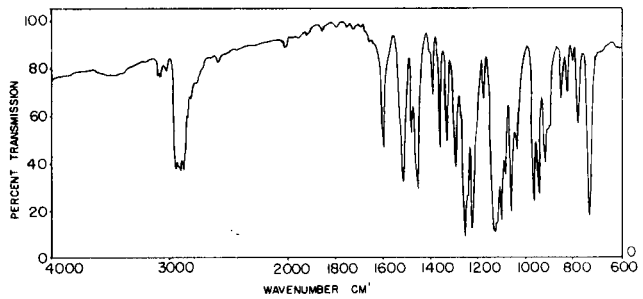

Figure 3. Infrared spectrum of Dibenzo-24-crown-8, polymorph-β (potassium bromide pellet).

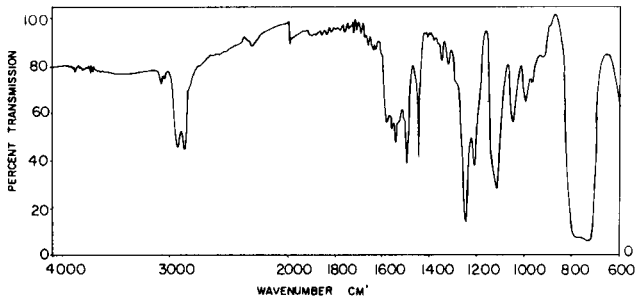

Figure 4. Infrared Spectrum of Dibenzo-24-crown-8, polymorph-α (in carbon tetrachloride). Identical to spectrum of polymorph-β (in carbon tetrachloride).

(*vide infra*). The origional sample of 4-*t*-butylbenzo-15-crown-5 was found to have a melting point of 97-98° rather than the origionally reported value of 43.5-44.5°, and its infrared spectrum was found to be identical with that of our product.

Polymorphic Behavior.

Satisfactory characterization of dibenzo-24-crown-8 is furthur complicated by the previously unreported polymorphic nature of this material. To date we have identified two crystalline forms which we have designated α and β, and a third form which we believe is a glass. The combination of the erroneously reported melting points and the existence of several polymorphs, each with its own distinctly different infrared spectrum, has led to considerable confusion. The infrared spectra of the two crystalline forms, α (Figure 2) and β (Figure 3), are most easily identified by the distinct differences in the carbon-hydrogen stretching area between 2800 cm^{-1} and 3100 cm^{-1} (although many other significant differences also are apparent).

It was origionally thought that the β polymorph simply contained benzene of crystallization, however heating the material to 160° for several minutes below a cold finger produced no residue on the cold finger. More conclusively, the nmr and ir spectra of both polymorphs in carbon tetrachloride showed both to be identical in solution.

Polymorph-β can be converted to polymorph-α by heating for several minutes at temperatures slightly above 78° which is the temperature at which rearrangement to polymorph-α begins (Figure 5). It is interesting to note

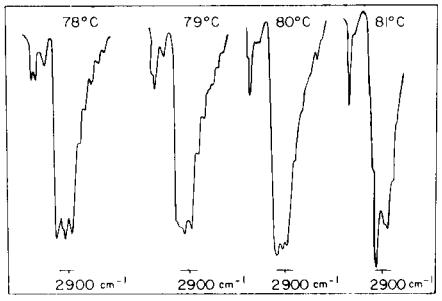

Figure 5. Thermal Conversion of Polymorph-β to polymorph-α. Samples were heated for 2.5 minutes at the temperature indicated. Spectra were obtained as potassium bromide pellets.

that even under a magnifying glass no disturbance of the crystals can be observed during the conversion. This would seem to indicate that the two forms are only slightly different conformers in the lattice. Polymorph-α can also be converted to polymorph-β by careful recrystallization from a dilute benzene solution, or preferably by seeding the solution with a small crystal of polymorph-β before crystallization begins.

When samples of dibenzo-24-crown-8 are melted and then cooled very rapidly, a third polymorph is obtained. This form is a hard waxy material. Its infrared spectrum in potassium bromide is somewhat variable and usually shows contamination by varying amounts of polymorph-α. In most respects however its spectrum is much simpler than that of either the α or β polymorph and is nearly identical with that of dibenzo-24-crown-8 in solution (Figure 4). These observations, along with the manner in which the material is prepared have led us to the conclusion that it is a glass.

It should be noted that this is not the first report of a crown ether exhibiting polymorphic behavior. *Cis-anti-cis*-dicyclohexano-18-crown-6 is known to exist as two different polymorphs (8). In that case however each form has a different melting point.

EXPERIMENTAL

All infrared spectra were obtained with a Beckman Acculab I infrared spectrophotometer.

Melting Points.

All melting points were determined using a Thomas Hoover melting point apparatus which was heated at two degrees per minute. The samples were placed in the bath at 5° below the anticipated melting point. In this manner the following values were obtained.

	Dibenzo-24-crown-8	4-*t*-Bultylbenzo-15-crown-5
Pedersen Sample	102.7-103.9	97-98
Parish Chemical Sample	102.3-103.4	96-98
50:50 mixture of Pedersen and Parish Samples	102.5-103.7	96-98

Thermal Conversion of Polymorph-β to Polymorph-α.

A Thomas Hoover melting point apparatus was adjusted to a constant temperature and samples of polymorph-β in glass capillaries were incubated for 2.5 minutes. Conversion to polymorph-α was monitored by preparing a potassium bromide pellet of the incubated sample and observing the infrared spectrum between 2700 cm^{-1} and 3100 cm^{-1}. At temperatures below 78° no conversion was observed and at temperatures above 81° total conversion occured. At 78° only minor change was observed and at 80° nearly total conversion was observed.

Acknowledgement.

Sincere thanks is extended to Dr. C. J. Pedersen without whose wholehearted cooperation, confirmation of the correct melting points could not have been obtained.

REFERENCES AND NOTES

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(4) Previously unpublished results, This laboratory.

(5) Personal Communication, Jerald S. Bradshaw, Brigham Young University, Provo UT.

(6) Personal Communication, Milton W. Davis, University of South Carolina, Columbia SC.

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