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LOW-TEMPERATURE OPTICAL ROTATORY DISPERSION

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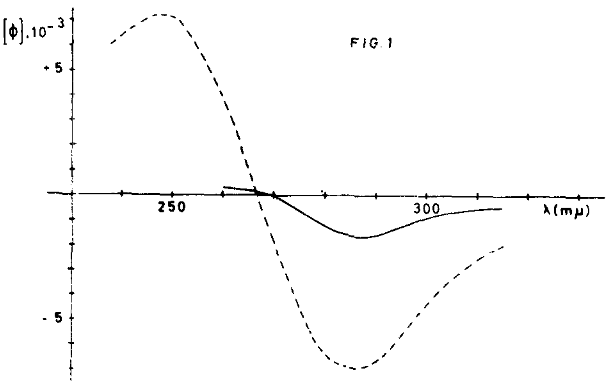
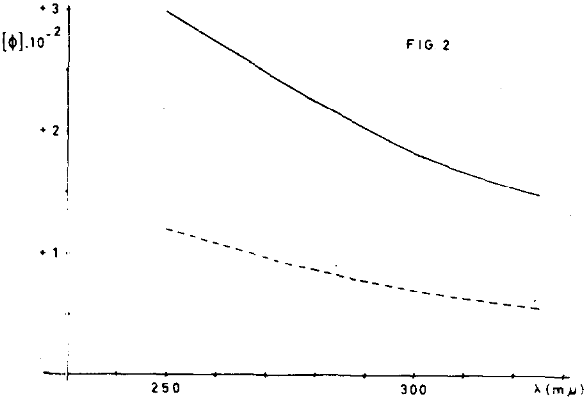
Optical rotatory dispersion (ORD) and circular dichroïsm (CD) are two closely connected phenomena that have found widespread use in organic chemistry. From the knowledge of one of them over the entire spectral range, the other can be calculated with the aid of the Kramers-Kronig relations. Since only a limited part of the spectrum lies within the range of present-day instruments, a combined use of ORD and CD is necessary for obtaining a maximum of information. In recent years several authors have shown that variable-temperature CD measurements can be of great help in the study of conformational and solvation equilibria (1). In the present letter a technique for measuring ORD at variable temperatures is reported, the lowest temperature attainable being -185°C (high-temperature ORD measurements have already been reported, e.g. (2)). At the present time the greater sensitivity of spectropolarimeters as compared to commercially available CD instruments is an advantage, if small effects have to be studied.

It is of vital importance to avoid all birefringence and depolarization in the lightpath. To this end we have chosen a construction in which a strain-free cylindrical quartz cell is cooled in a stream of nitrogen. The cell is surrounded by an insulating vessel. The light passes through holes in the vessel that are closed by quartz windows, which are connected to the walls of the vessel very loosely, so that no strain is introduced. To avoid condensation of water on the windows, these are heated by a heating wire, fitted in the brass housing of the windows. Temperatures from -185°C to -100°C are obtained by heating resistances below or above the liquid nitrogen level in the vessel. By blowing precooled nitrogen into the vessel the temperature range from -100°C upward



Molecular rotation of (–)α-phellandrene
in MIP at 20°C (---) and at -150°C (——).



Molecular rotation of (+) butanol-2
in EPA at 20°C (---) and at -150°C (——).

is easily accessible. The same technique can also be employed for measuring variable temperature CD and absorption spectra.

As an illustration of the potentialities of this technique the low-temperature ORD curves of (-)α-phellandrene in MIP (1 methylcyclohexane, 4 isopentane) and of (+) butanol-2 in EPA (5 ether, 5 isopentane, 2 alcohol) are shown (fig. 1 and 2). The concentrations have been corrected for volume contraction. It may be noted that (-)α-phellandrene at low temperatures presents a case, where CD measurements can not be performed with any accuracy. Of both compounds the high-temperature rotations at one wavelength have already been reported (3, 4). The variations in rotation with temperature, which show the same trends as in the measurements reported in this letter, were explained as due to displacements in conformational equilibria.

Full details of the technique and a discussion of these and other results will be published shortly.

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