The "Naphtodioxanes"
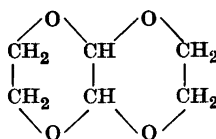
M. DANØ, S. FURBERG and O. HASSEL

*Universitetets Kjemiske Institutt,
Blindern — Oslo, Norway*

$$\begin{array}{ccc} O & O \\ CH_2 & CH & CH_2 \\ CH_2 & CH & CH_2 \\ O & O \end{array}$$

Of the two "naphtodioxanes" prepared from 2,3-dichlorodioxane and glycol, the lower melting isomer (m. p. 111°) is reported to have a considerable dipole moment (1.9 D.), whereas the moment of the isomer of m. p. 136° is found to be rather small (0.7 D.) [1]. The substances were thought to have the structure formula

and thus to be stereoisomeric and corresponding to the two decalins, and movable forms of the cyclohexane ring had therefore to be considered in order to explain the observed dipole moments [1]. The knowledge more recently obtained about the shape of the decalin molecules [2] has, however, made us doubt the correctness of this explanation, and we have therefore carried out some investigations of the two naphtodioxanes in our laboratory.

The coloured solution of steel II was kept for some time for observation purposes. After a lapse of two weeks the extinction was measured to 0.256. After filtration the same value was measured. The day afterwards a white precipitate began to form.

B. The stability of the colouring reagent was examined by measurements taken over a period of 9 weeks on the same steel solutions. The variations were insignificant and non-systematic:

Table 2.

Obs. time Weeks	Colour extinction less blank extinction		
	I	II ·	III
9	.199 $\pm$ .001	.255 $\pm$ .001	.323 $\begin{array}{c}+\,.001\\ \div\,.002\end{array}$

When the colouring reagent had aged for about 2 weeks it became possible to detect hydrogen disulphide by placing a strip of filter paper wetted with lead acetate solution in the neck of the reagent bottle; the evolution was slow, however, and did not upset the measurements.

C. Because of the price of butyl cellosolve a "blank reagent 2" was made in which the butyl cellosolve was entirely omitted and replaced with water. The two types gave exactly the same values.

In the course of a few days the "blank reagent 2" began to evolve hydrogen disulphide.

In Table 3 shows the connection between "% molybdenum in the interval 0—1 %" and "colour extinction less blank extinction".

Table 3.

% Mo	0	.09(3)	.18(5)	.24	.28	.37	.65	1.00
Extinction	.002	.075	.126	.162	.176	0.200	.255	.323

Seemingly the curve begins by being nearly straight, then bends through a transition zone into another straight line. This unusual aspect may be caused by different dominating colour complexes at lower and higher molybdenum contents.

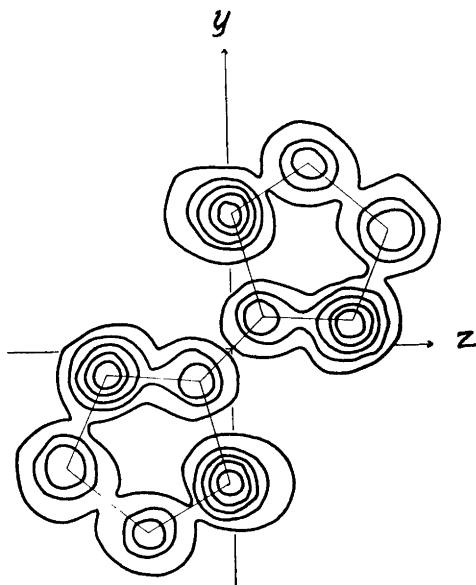1. Kapron, X., and Hehman, X. *Ind. Eng. Chem.* **17** (1945) 573.

Fig. 1. Fourier projection in the direction of the a-axis.

The higher melting isomer. A few measurements of the dielectric properties of this substance indicate a lower value of the dipole moment than reported by Henriquez [1]. It seems possible that the moment may in fact be zero. This would seem to indicate that the molecule may correspond to *trans* or *cis* decalin, the former demanding a zero moment, the latter probably a very small one.

The crystals of this isomer are monoclinic with $a = 11.55$ Å, $b = 7.04$ Å, $c = 15.88$ Å and $\beta = 92.5°$. Density: 1.46 g/cm^3 (calc. 1.50 g/cm^3). The unit cell contains eight molecules and the space group is either $A2/a$ or Aa. The crystals do not appear to be piezoelectric (Blomgren [3]), and the former is therefore the most probable one. A complete structure determination would in all cases demand a considerable amount of work, as the space groups in question do not require any symmetry of the individual molecules.

The lower melting isomer. This compound proved to be much better suited for an X-ray structure analysis. The crystals are monoclinic with the following lattice constants: $a = 4.46$ Å, $b = 7.76$ Å, $c = 11.64$ Å and $\beta = 122°$. The observed density is 1.40 g/cm^3 (calc. 1.42 g/cm^3), and there are only *two* molecules in the unit cell. The space group is $P2_1/c$, from which follows that the molecules must be centrosymmetrical. Although the dipole moment observed in solution would seem to exclude the possibility of molecules corresponding to those of *trans* decalin, a structure determination based on such a model was attempted. We found, however, that it was impossible to obtain a satisfactory agreement between observed and calculated intensities in this way. The assumption was therefore made that the structural formula

$$\begin{array}{ccc} CH_2-O\diagdown & & \diagup O-CH_2 \\ | & CH-CH & | \\ CH_2-O\diagup & & \diagdown O-CH_2 \end{array}$$
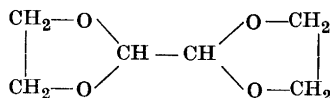
might be the correct one. This possibility was discussed also by Böeseken *et al.*, but rejected mainly on chemical grounds. However, good agreement with the experimental intensities was soon obtained when this formula was assumed. In Fig. 1 the electron density map corresponding to a projection along the short axis is reproduced, and it shows, we think, with certainty that the compound actually has the formula given above, and should be described not as "naphtodioxane", but as bi-1,3-dioxacyclopentyl (2). The dipole moment observed in solution is thus satisfactorily accounted for.

Full details of the crystal structure determination will be given later.

1. Böeseken, J., Tellegen, F., and Cohen Henriquez, P. *Recueil* **54** (1935) 733.
2. Bastiansen, O., and Hassel, O. *Tids. Kjemi, Bergvesen, Metallurgi.* **6** (1946) 70.
3. E. Blomgren. Private communication.