DIPOLE MOMENT AND STRUCTURE OF TRIOXANE

By Arthur A. Maryott and S. F. Acree

ABSTRACT

Trioxane is a solid polymer of formaldehyde resembling the well-known solvent
dioxane in its chemical properties. The molecule can possibly exist in two spaci-
ally different forms resembling a chair and a cradle, for which the theoretical dipole
moments are 2.3 and 0.6×10^{-18} electrostatic unit (esu), respectively. The experi-
mental value in benzene was found to be 2.18×10^{-18} esu. Hence it is concluded
that ordinary trioxane is largely in the chair form, possibly in equilibrium with
a small amount of the cradle form. This cyclic ether would therefore be suitable
for mixing with nonpolar solvents to study the effect of increased polarity on the
activities and absorption spectra of indicators.

CONTENTS

I. INTRODUCTION

Trioxane, frequently called α-trioxymethylene, is a cyclic trimer of
formaldehyde. Its physical and chemical properties have been dis-
cussed by Walker and Carlisle [1].[1] Studies of Raman spectra [2] and
crystal structure [3] indicate that it has a puckered, six-membered ring
structure analogous to that of cyclohexane. Consequently, it may
exist in two stereo isomeric forms, as discussed by Sachse [4] and by
Mohr [5]. They are usually designated as the "chair," or Z, and the
"cradle," or C forms.

Until recently the structure of cyclohexane and other six-membered
monocyclic compounds was open to doubt. Chemical evidence based
upon the Thorpe-Ingold hypothesis of valency deflection [6] indicated
considerable strain in the cyclohexane ring and suggested a planar
structure. On the other hand, the Sachse-Mohr theory of strainless
rings required that these cyclic compounds have a puckered or multi-
planar configuration and may exist in at least two isomeric forms.
The isolation of two stable forms of decahydronaphthalene [7] cor-
responding to the "chair" and "cradle" structures confirmed the
Sachse-Mohr theory for bicyclic compounds. Since then such
isomerism has been demonstrated in a number of other bicyclic and
polycyclic compounds. However, despite numerous attempts to
isolate two such forms of cyclohexane derivatives and other mono-

[1] Figures in brackets indicate the literature references at the end of this article.

cyclic compounds, there is no authentic proof of the separate existence of any such isomeric forms. Apparently, the strain of valency angles involved in passing from one of the strainless forms to the other is not sufficiently great to prevent rapid conversion of one to the other. Stability of the two isomers of decahydronaphthalene is supplied by the interlocking ring system, which prevents change of the two forms into each other without rupture of a covalent bond. One might expect that under ordinary conditions many six-membered monocyclic compounds would exist as equilibrium mixtures of the "chair" and "cradle" forms. It appears, however, that such a mixture containing appreciable amounts of both forms has been established only in the case of cyclohexane-1,4-dione.

The dipole moment of this compound in benzene solution has been found to be 1.3 D^2 [8]. This value is intermediate between that calculated for the "chair" ($\mu=0$) and the "cradle" ($\mu=3.9$ D) forms and corresponds to an equilibrium mixture containing about 10 percent of the "cradle" form. In the case of heterocyclic compounds, such as dioxane, paraldehyde, and morpholine, as well as cyclohexane and its derivatives, definite evidence for the existence of the "chair" form alone has been obtained. The isolation of two forms of methylcyclohexane corresponding to the two possible multiplanar structures has been claimed recently [9] but conclusive proof is lacking.

To determine whether the "chair" or the "cradle" form is the stable one in solution at ordinary temperatures or whether the solution consists of an equilibrium mixture of the two forms, the dipole moment of trioxane has been measured using benzene as solvent. With trioxane, the "chair" form would have a fairly large dipole moment, whereas the "cradle" structure would have only a small moment. The experimental data give a dipole moment of 2.18 D for trioxane.

II. EXPERIMENTAL METHODS AND RESULTS

Trioxane obtained from E. I. du Pont de Nemours & Co. Inc., was recrystallized from cyclohexane and then sublimed. The melting point was 61° C. The benzene, of analytical grade, was distilled immediately before use.

A heterodyne beat method was used for the measurement of the dielectric constants. The cell was a specially designed glass vessel with silver-mirror surfaces to serve as plates. Measurements were made in an air bath regulated at 30°±0.02° C.

The experimental data are listed in table 1. The molar polarization of the solute at infinite dilution, P_2^∞, is calculated from the Hedestrand equation [10],

$$P_2^\infty = \frac{3P_1}{(\epsilon_1-1)(\epsilon_1+2)} \frac{\Delta\epsilon}{f_2} - \frac{P_1}{d_1} \frac{\Delta d}{f_2} + P_1\frac{M_2}{M_1}.$$

Wherever used, the subscripts 1, 2, and 12 refer to the pure solvent, solute, and solution, respectively, f expresses the concentration in mole fraction, ϵ represents the dielectric constant, d is the density, and M is the molecular weight. $\Delta\epsilon$ equals $\epsilon_{12}-\epsilon_1$, and Δd equals $d_{12}-d_1$.P_1, the molar polarization of the solvent, is defined as

2 D (Debye) = 10^{-18} esu.

$$\frac{\epsilon_1 - 1}{\epsilon_1 + 2} \frac{M_1}{d_1}.$$

The above equation reduces to

$$P_2^{\infty} = 14.86 \frac{\Delta \epsilon}{f_2} - 30.67 \frac{\Delta d}{f_2} + 0.3412 \ M_2$$

when the numerical values for the constants of the solvent are inserted. The dielectric constant and density of pure benzene at 30° C were taken as 2.2627 and 0.8684, respectively. P_E is the electronic polarization obtained by summation of the atomic refractivities listed in Landolt-Bornstein Tabellen. The dipole moment was calculated from the relation

$$\mu = 0.223 \ (P_2^{\infty} - P_E)^{\frac{1}{2}} \times 10^{-18} \text{ esu.}$$

TABLE 1.—*Mole fraction, f_2, increment of dielectric constant, $\Delta\epsilon$, and dipole moment, μ, of trioxane*

f_2	$\Delta\epsilon$
0.00448	0.0276
.01083	.0671
.01695	.1054
.02155	.1342
.02443	.1516

$\Delta\epsilon/f_2 = 6.20$
$\Delta d/f_2 = 0.283$
$P_2^{\infty} = 114.4$
$P_E = 18.8$
$\mu = 2.18 \times 10^{-18}$ esu.

III. DISCUSSION

The two possible isomeric structures for trioxane are illustrated in figure 1. The "chair" form has an axis of symmetry perpendicular to the plane of the three carbon atoms. The three oxygen atoms lie in a plane parallel to and slightly below this plane. Calculation of the dipole moment of the "chair" form by vector addition of the bond moments gives 2.3 D if the C—O and C—H bond moments are taken as 0.9 D and 0.2 D, respectively, and all of the valence angles are assumed to be tetrahedral. The moment calculated for the "cradle" form is 0.6 D. In view of the necessarily rather approximate nature of the calculated moment, the agreement between the actual value of 2.18 D and that calculated for the "chair" form is as good as could be expected. The presence of a small amount of the practically nonpolar "cradle" form, however, is not excluded.

Trioxane is closely related structurally to the more familiar paraldehyde, which is a cyclic trimer of acetaldehyde containing alternate carbon and oxygen atoms in the ring and differing from trioxane only in that one hydrogen of each methylene group has been replaced by a methyl group. Unlike trioxane, however, which has only one possible structure for each of the two Sachse-Mohr forms, paraldehyde has four possible stereoisomeric structures for the "chair" and for the "cradle" configurations. Electron diffraction studies [11] of paraldehyde vapor are in favor of a "chair" structure, in which the

three methyl groups are symmetrically located in a plane parallel to and close to the plane formed by the three carbon atoms of the ring, and in which all the valence angles are approximately tetrahedral. The dipole moment of paraldehyde has been found to be 2.03 D [12] in benzene solution. Although this value is somewhat lower than that found for trioxane, whereas a slightly higher value might be expected because of induction effects in the methyl groups, it does lend support to a "chair" structure for the molecule.

The cyclic ether, trioxane, in the molten state or mixed in various proportions with other solvents, would have very useful solvent properties somewhat similar to those of dioxane. It can be dissolved in varying amounts in nonpolar solvents to increase polarity, and in this connection should prove of interest in investigations on the effect of various polar and nonpolar organic compounds and solvents on the absorption spectra of indicators and their changes by organic acids and bases.

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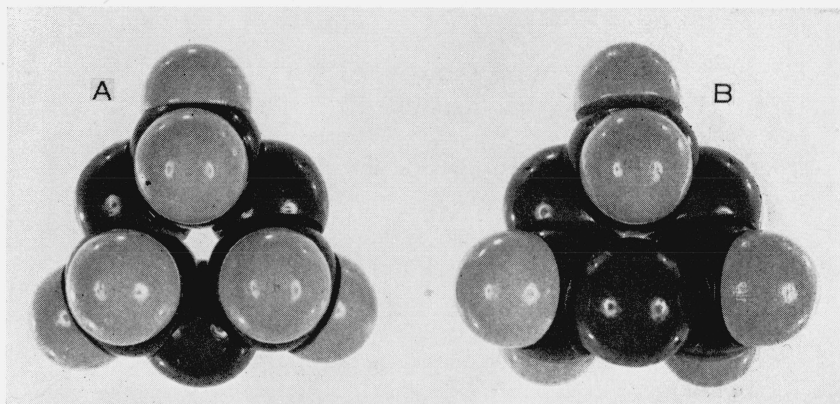
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FIGURE 1.—*Chair (A) and cradle (B) configurations of trioxane.*

Two hydrogens (light colored atom models) are attached to each carbon (black models). The other atom
models are the oxygens connecting the carbons.

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