[010]. Absorption corrections were applied to the intensities including 1068 observed and 426 unobserved reflexions. Least squares refinements led to an R value of 6.86 %. For the evaluation of TIE molecular parameters only an approximate correction for rigid body motion was feasible, due to the small number of atoms in the molecule. When evaluating the $N-I$ bond distance -2.979 Å — the structure of the pyrazine molecule was assumed to be that reported by Wheatley.[3] The lengths of the diagonals of the iodine parallelogram of TIE were found equal to 5.093, resp. 5.074 Å. The first value is the distance between iodine atoms linked to nitrogen. Distances between nearest, non-equivalent iodine atoms are 3.638, resp. 3.551 Å, values compatible with electron diffraction results.[4]

The packing of the TIE molecules is almost identical in the TIE crystal and in the pyrazine compound. The angle between the $N-I$ bond direction and the pyrazine plane is 172.7°.

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The Energy Difference between the Chair and Skew-Boat Forms of the 1,3-Dioxane Ring

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This paper reports an estimation of the energy difference between the chair and skew-boat forms of the 1,3-dioxane ring.

Delmau and Duplan[1] recently concluded that 4-methyl-4-t-butyl-1,3-dioxane exists in the skew-boat form on the basis of NMR experiments and assumed further that also 4,4-dimethyl-, 4,4,5-trimethyl-, and 4,4,6-trimethyl-1,3-dioxanes are skewboat forms.

Kinetic conformational analysis led this writer[2] to the conclusion that methyl-substituted 1,3-dioxanes with an axial methyl group at position 2, 4, or 6 do not exist in the skew-boat form, whereas methyl-substituted 1,3-dioxanes with two or three axial methyl groups at positions 2, 4, and 6 may well have stable flexible forms. The interaction energy of an axial methyl group at position 5[3,4] is about 0.8 kcal/mole because it interacts only slightly with the "axial" electron pairs of the two oxygen atoms.

Anderson et al.[5] observed that the NMR spectra of 4-methyl-, 4,4-dimethyl-, 2,2-dimethyl-, 2,2,5,5-tetramethyl-, and 2,cis-4,$trans$-6-triphenyl-1,3-dioxanes are in agreement with a chair form of the ring in these compounds. Delmau[6] reinvestigated his spectra and came to the same conclusion.

Both Anderson et al.[5] and Riddell and Robinson[4] postulated that the free energy difference between the chair and skew-boat forms of the 1,3-dioxane ring must be greater than 3 kcal/mole, and probably close to that between the corresponding forms of the cyclohexane ring. The enthalpy difference, $\Delta H_{c\rightarrow s}$, between the chair and skew-boat forms of the 1,3-dioxane ring (Fig. 1) has been estimated, employing the simple approximation used for cyclohexane,[7] to be twice the barrier to internal rotation in methanol (1.11 kcal/mole[9]), i.e. about 2.2 kcal/mole.[8] Riddell and Robinson[4] assumed that the barrier to internal rotation (2.72 $\pm$ 0.14 kcal/mole[10]) in dimethyl ether is a better approximation, since the barriers to internal rotation about
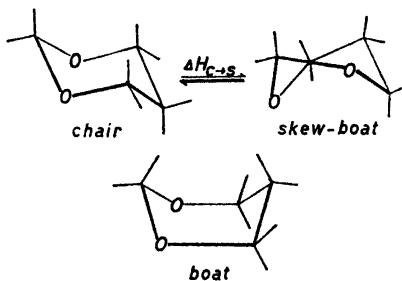

Fig. 1. The different conformations of the 1,3-dioxane ring.

Table 1. Physical constants and heats of formation of isomeric 2,2,4,6-tetramethyl-1,3-dioxanes.

Isomer	b.p./torr	n_D^{25}	d_4^{25}	$-\Delta H_f°$(liq.), kcal/mole
(±)-*trans*	131.5—132.5°/760	1.4126	0.8939	126.03 ± 0.50
cis	137.9°/719	1.4175	0.9014	129.38 ± 0.50

C—O bonds in CH_3—OX molecules, unlike the barriers to internal rotation about C—C bonds in CH_3—CH_2X molecules, are sensitive to the nature of the group X. Consequently, the barrier to internal rotation in 1,3-dioxane (Fig. 1) is about 5.44 ± 0.28 kcal/mole.

Pihlaja and Luoma[11] established recently that the interaction energy of an axial methyl group at position 2 in the 1,3-dioxane ring is 4.13 kcal/mole.[2,12] When it is taken into account that 2,2-dimethyl-1,3-dioxane exists predominantly in the chair form,[5] the free energy of its skew-boat form must be about 4.13 + RT ln 19 = 4.13 + 1.75 = 5.88 kcal/mole higher than that of the chair form assuming that the proportion of the latter at equilibrium is at least 95 %.

The heats of formation of isomeric 2,2,4,6-tetramethyl-1,3-dioxanes (Table 1) differ by 3.35 kcal/mole. *cis*-2,2,4,6-Tetramethyl-1,3-dioxane (I) exists predominantly in the chair form (Fig. 2),[2,5,13] whereas there is a strong interaction of the axial methyl groups at positions 2 and 6 in the chair form (II) of (±)-*trans*-2,2,4,6-tetramethyl-1,3-dioxane. The magnitude of this diaxial interaction, 8.9 kcal/mole, was evaluated by this author previously.[2,13]
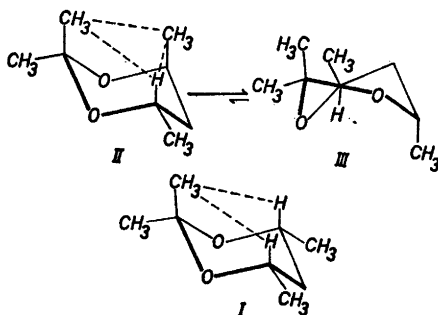

Fig. 2. The chair forms of *cis*- and *trans*-2,2,4,6-tetramethyl-1,3-dioxanes (I and II) and the stable skew-boat form of the latter (III).

It was concluded earlier[2] on the basis of kinetic and combustion data, that the *trans* isomer has the skew-boat form (III) in which, of the diaxial interactions in the chair form, only about 0.6 kcal/mole remains.

The total interaction energies of the structures I and II (Fig. 2) have the following values:

$$(\textstyle\sum E_i)^{\mathrm{I}} = H_{2a}{}^i = 4.13 \text{ kcal/mole}$$
$$(\textstyle\sum E_i)^{\mathrm{II}} = \tfrac{1}{2}H_{2a}{}^i + H^i_{2a\text{-Me} \leftrightarrow 4a\text{-H}} +$$
$$+ H^i_{2a\text{-Me} \leftrightarrow 6a\text{-Me}} = 2.06 + 1.0 +$$
$$+ 8.9 = 11.96 \text{ kcal/mole}$$

where the values of H^i were taken from Refs. 2 and 10. Thus $\Delta E_i = 7.83$ kcal/mole. When II changes to III, an energy relief $E_r = 11.96 - 0.6 = 11.36$ kcal/mole results. Now we can evaluate the enthalpy difference for the equilibrium in Fig. 1, since

$$\Delta H_{\mathrm{c} \rightarrow \mathrm{s}} = \Delta H_{\mathrm{I} \rightleftharpoons \mathrm{III}} + E_r - \Delta E_i = 3.35 + 11.36 - 7.83 = 6.88 \text{ kcal/mole}.$$

It was shown previously[2] that the excess entropy of the skew-boat form is 3.9 ± 0.5 cal/degr. mole and hence

$$\Delta G_{\mathrm{c} \rightarrow \mathrm{s}} = 5.72 \pm 0.15 \text{ kcal/mole},$$

and thus in good agreement with the other two estimates, when it is assumed that the first estimate represents most likely a free energy difference. The above estimation can be made also more simply, since the total excess entropy of (±)-*trans*-2,2,4,6-tetramethyl-1,3-dioxane is

$$\Delta S_{trans} = 3.9 + 1.4 \text{ cal/degr. mole}$$

where the first term is due to the skew-boat form and the latter to the (±)-forms. Consequently

$$\Delta G_{\mathrm{c} \rightarrow \mathrm{s}} = 3.35 + 4.13 - 0.3 \times 5.3$$
$$= 5.9 \pm 0.7 \text{ kcal/mole}.$$

The above considerations lead to the following values of the energy terms for the equilibrium in Fig. 1: Table 2.

Table 2.

$\Delta H°$, kcal/mole	$\Delta S°$, E.U.	$\Delta G°$, kcal/mole
7.1 ± 0.8	3.9 ± 0.5	5.9 ± 0.7
6.5 ± 0.9	»	5.3 ± 1.0
7.0 ± 0.6	»	5.9 ± 0.4
6.6 ± 0.4	»	5.4 ± 0.3
Mean 6.8 ± 0.7	3.9 ± 0.5	5.6 ± 0.6

The enthalpy difference is close to that between the chair and boat forms of the cyclohexane ring, but it is obvious that the energy difference between the boat and skew-boat forms of 1,3-dioxane is less than that between these two forms of cyclohexane (1.6 kcal/mole [14]).

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