

Relation between Crystal Structures of Tetraiodoethylene and its 1:1 Pyrazine Compound

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A striking example of virtually identical packing of molecules in a one-component crystal and in one of its addition compounds is provided by tetrabromoethylene (TBE) and its 1:1 pyrazine adduct.¹ Similar, but not identical behavior is found in the tetraiodoethylene (TIE)-pyrazine system. In the 1:1 TIE-pyrazine crystal *two* sets of infinite chains of alternating donor and acceptor molecules are present, running in the directions [111], resp. [111], (cf. Fig. 1) with a nitrogen-halogen bond distance — 2.98 Å — slightly shorter than that observed in the corresponding TBE-pyrazine crystal (3.02 Å). Formally, both crystal structures may be derived from the

(isomorphous) TBE¹ and TIE² structures by removal of half the number of their molecules and introducing a corresponding number of pyrazine molecules. In the TBE case the pyrazine molecules occupy centrosymmetrical lattice sites from which acceptor molecules have been removed, in the TIE adduct, however, sites vacant in the TIE crystal are used. Although belonging to the same space group ($P2_1/c$) the two 1:1 addition compounds are therefore not isomorphous.

The crystallographic parameters of the TIE and the TIE-pyrazine compounds are:

	TIE ²	TIE-pyrazine
<i>a</i> (Å)	15.10 ± 0.05	12.371 ± 0.003
<i>b</i> (Å)	4.45 ± 0.02	4.472 ± 0.006
<i>c</i> (Å)	13.00 ± 0.04	12.676 ± 0.007
β (°)	109 ± 1	117.57 ± 0.03

The TIE-pyrazine structure was derived from three-dimensional X-ray data (MoK-radiation) collected from integrated Weissenberg diagrams with rotation about

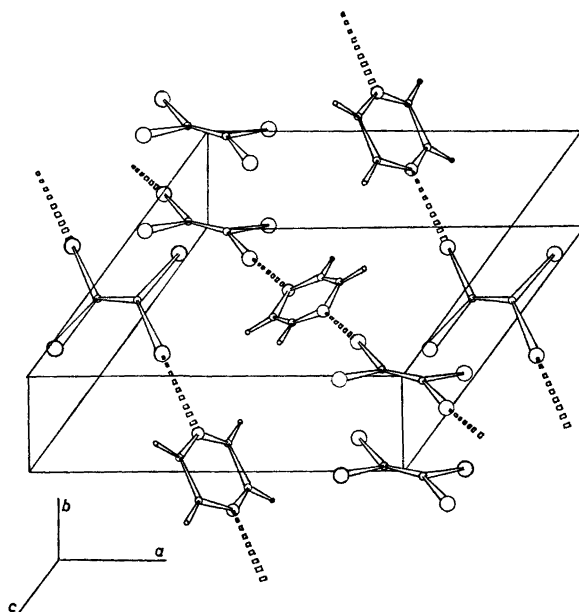


Fig. 1.

[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 Duplan¹ 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 writer² 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. Delmau⁶ reinvestigated his spectra and came to the same conclusion.

Both Anderson *et al.*⁵ and Riddell and Robinson⁴ 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/mole⁹), *i.e.* about 2.2 kcal/mole.⁸ Riddell and Robinson⁴ assumed that the barrier to internal rotation (2.72 ± 0.14 kcal/mole¹⁰) in dimethyl ether is a better approximation, since the barriers to internal rotation about

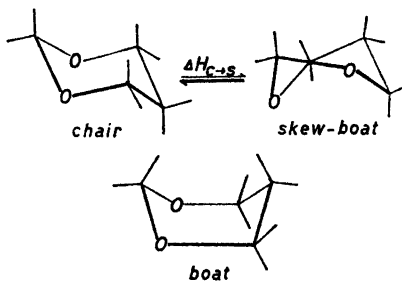


Fig. 1. The different conformations of the 1,3-dioxane ring.