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MOLECULAR STRUCTURE AND CONFORMATION OF SOME DIHALOGENODIOXANES[1]

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IN recent years the properties and the conformational relationships of some dihalogenocyclohexanes and dihalogenodecalins have been studied in this laboratory.[2,3,4] In the present communication we summarize the results obtained in extending the investigations to halogeno-substituted dioxanes.

Monochlorodioxane, the known dihalogenodioxanes and one 2,3,5,6-tetrachlorodioxane were synthesized (see Table 1) and studied.

The following methods were employed for the investigation of the conformational characteristics of the dihalogenodioxanes:

(1) Dipole moments were calculated from measurements in dilute solutions

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[1] Details will be published in the thesis of C. Altona, Leiden and in forthcoming publications in Rec. Trav. Chim. The results of the X-ray analyses will be published in Acta Cryst.

[2] W. Kwestroo, F. A. Meyer and E. Havinga, Rec. Trav. Chim. **73**, 717 (1954).

[3] W. Kwestroo, Thesis, Leiden (1954).

[4] J. A. van der Linden, Thesis, Leiden (1958).

TABLE 1. Dipole moments of some halogeno-substituted dioxanes

XX	Compound	Melting point	Dipole moment in benzene	(Debyes) in CCl_4
I	Monochlorodioxane[5]		2.24	2.28
II	Trans-2,3-dichlorodioxane[6]	31	1.63	1.62
III	Trans-2,3-dibromodioxane[7]	74	1.90	1.86
IV	Cis-2,3-dichlorodioxane[6]	54	3.06	3.00
V	Trans-2,5-dichlorodioxane[8]	124	0.6	0.6
VI	Trans-2,5-dibromodioxane[9]	86 - 100 (decomp.)	0.8	
VII	2,3,5,6,-Tetrachlorodioxane[10]			

in benzene and carbon tetrachloride, using the extrapolation formulas of Halverstadt and Kumler.[11]

(2) Infra-red absorption spectra were obtained from the compounds in the solid state (KBr-disks) and from solutions in carbon disulphide; the spectrum of III was also measured in cyclohexane and the spectrum of II in cyclohexane and nitromethane.

(3) Raman spectra were taken of solutions of II, III and IV in solvents with dielectric constants varying from 2.1 to 37.5.

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[5] R. K. Summerbell and L. N. Bauer, *J. Amer. Chem. Soc.* **57**, 2364 (1935).

[6] R. K. Summerbell and H. E. Lunk, *J. Amer. Chem. Soc.* **79**, 4802 (1957).

[7] H. C. Dehm, *J. Org. Chem.* 147 (1958).

[8] L. A. Bryan, W. M. Smedley and R. K. Summerbell, *J. Amer. Chem. Soc.* **72**, 2206 (1950).

[9] R. K. Summerbell and L. K. Rochen, *J. Amer. Chem. Soc.* **63**, 3241 (1941).

[10] M. Udicke and W. Stumpf, *Naturwissenschaften* **40**, 363 (1953).

[11] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.* **64**, 2988 (1942).

(4) X-ray diffraction patterns were taken of single crystals of III, IV, V and VII (see Table 2).

TABLE 2. Dimensions of the unit cells in Ångstrom units and space-groups of some halogenodioxanes

Dioxane derivatives		a	b	c	α	β	γ	n	Space-group
III	Trans-2,3-dibromo-	5.68	7.63	16.02	90	90	90	4	$P2_12_12_1$
IV	Cis-2,3-dichloro-	4.52	10.75	13.12	90	90	90	4	$P\ 2_1/n$
V	Trans-2,5-dichloro-	4.58	5.46	6.56	86	102.5	107	1	P i
VII	2,3,5,6-tetrachloro-	6.70	7.60	$\frac{7.52}{\sin\beta}$	90		90	2	$P\ 2_1/c$

The analyses of the structure of III and V are in the stage of refinement; they confirm that both compounds are trans-substituted and that the dioxane ring has the chair conformation. To our surprise the halogen atoms of both compounds were found to occupy axial positions.

As is well known, the trans-1,2- and the trans-1,4-dihalogenocyclohexanes occur in solution as an equilibrium mixture consisting mainly of two conformations, the diaxial (aa) and the diequatorial (ee) chair conformations. This equilibrium varies with the solvent, as is evident from the solvent-dependent dipole moments in the case of the 1,2-trans-substituted compounds and from the solvent-dependent Raman spectra and infra-red absorption spectra of these substances.[2,3,12-16]

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[12] K. Kozima and T. Yoshino, J. Amer. Chem. Soc. **75**, 166 (1953); K. Kozima, K. Sakashita and S. Maeda, J. Amer. Chem. Soc. **76**, 1965 (1954).

The trans-substituted dihalogenodioxanes differ in these aspects from the cyclohexane analogues. The dipole moment appeared to be independent of the solvent. The infra-red spectra of these compounds in solution - regardless of the solvent - are in all cases identical with those of the crystals. The Raman spectra were also found not to vary with the solvent and to be practically identical with those obtained from the crystalline material.

No indications were found, then, for the occurrence of more than one conformation. We tentatively conclude that the molcules of the trans-dihalogenodioxanes show a strong preference for one of the possible conformations.

Taking into consideration that, according to the X-ray analyses, in solid III and V the halogen atoms are in aa positions, that the dipole moments of II and III do not differ appreciably and that the infra-red spectra of V and VI bear a close resemblance, we feel safe in concluding that the trans-2,3-dihalogeno- and the trans-2,5-dihalogenodioxanes occur in solution as well as in the solid state in the diaxial chair conformation.

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[13] A. Tulinskie, A. DiGiacomo and C.P. Smyth, J. Amer. Chem. Soc. **75**, 3552 (1953).

[14] P. Bender, D. L. Flowers and H. L. Goering, J. Amer. Chem. Soc. **77**, 3463 (1955).

[15] P. Klaeboe, J. J. Lothe and K. Lunde, Acta Chem. Scand. **11**, 1677 (1957).

[16] For an early discussion of infra-red data see also: M. Larnaudie, C. R. Acad. Sci., Paris **326**, 909 (1953). The results of investigations on the conformations of cyclohexane derivatives in the gaseous state by electron diffraction were summarized by O. Hassel, Research **3**, 504 (1950).

Cis-2,3-dichlorodioxane (IV) probably has the ea conformation, in accordance with the value for the dipole moment that is practically the same as that found for cis-1,2-dichlorocyclohexane (3.13 D[3]).

The dipole moments of II and III are somewhat higher than might be expected for a purely diaxial conformation. More data will be needed before a choice can be made between the several possible causes for this phenomenon.

As to the reasons why the halogen atoms preferentially occupy axial positions in the case of dihalogenodioxanes, it might be argued that with such compounds the interaction between the electrons of an equatorial halogen atom and those of the oxygen atom is relatively unfavourable. Furthermore, the number of axial hydrogen atoms that cause steric hindrance is, of course, smaller in the derivatives of dioxane than in the substituted cyclohexanes.