Structure and Rotational Isomerism of Ethane-1,2-dithiol; an Electron Diffraction Study

By ISTVÁN HARGITTAI* and GYÖRGY SCHULTZ

(*Centre for Studies on Chemical Structures, the Hungarian Academy of Sciences, Budapest, VIII, Puskin u.* 11-13, *Hungary*)

Summary Electron diffraction data show the existence of *anti*- and *gauche*-conformers around the C–C bond in ethane-1,2-dithiol vapour with relative abundances of 62 and 38%, respectively.

DESPITE extensive structural studies on other ethane derivatives, ethane-1,2-dithiol has been the subject only of a vibrational analysis by Hayashi *et al.*[1] In the present study we have investigated the rotational isomerism of ethane-1,2-dithiol in the vapour phase and also the molecular geometry for force-field studies.

Electron diffraction measurements were made with the Budapest apparatus using the new nozzle[2] and sector[3] systems. The nozzle temperature was *ca.* 70 °C, with nozzle to plate distances of *ca.* 50 and 20 cm; 60 keV electrons were used. Experimental molecular intensities were obtained in the range $1{\cdot}75 \leqslant s \leqslant 30{\cdot}25$ Å^{-1} ($s = 4\pi\lambda^{-1}\sin\frac{1}{2}\theta$).

The three peaks between 1 and 2 Å on the experimental radial distribution curve arise from the bond distances C–H, S–H, C–C, and S–C. The non-bonding S · · · C distances appear under the maximum at *ca.* 2·8 Å; these are not influenced by the rotation around the C–C bond. The major contributions for the maxima at *ca.* 3·5 and 4·5 Å

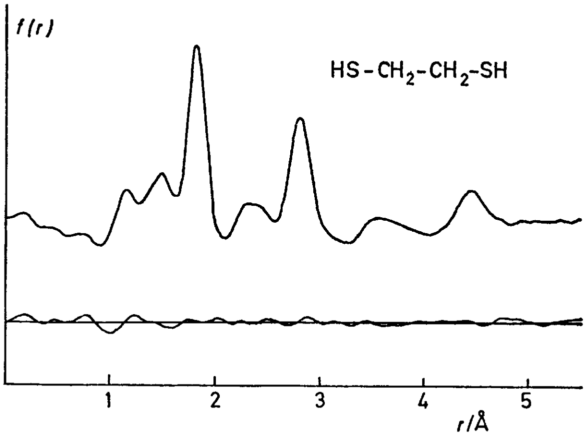

FIGURE. *Experimental radial distribution and difference curve between the experimental and theoretical distributions.*

come from the S ⋯ S non-bonding distances of the *gauche*- and *anti*-conformers, respectively.

If, assuming that the S–H bonds are *anti* to the C–C bonds,† the geometry of the *anti*-conformer around the C–C bond can be described by four bond lengths and four bond angles. In addition, the torsional angle for the *anti*-form, τ (S–C–C–S), is needed for determination of the geometry of the *gauche*-form.

Table

*Results (standard deviations in parentheses) of least-squares refinement of electron diffraction data for ethane-*1,2-*dithiol.*

	Parameters	
r(C–H)/Å	1·120	(0·009)
l(C–H)/Å	0·076	(0·010)
r(S–H)/Å	1·40	(0·02)
l(S–H)/Å	0·07	(0·04)
r(C–C)/Å	1·53	(0·02)
l(C–C)/Å	0·06	(0·03)
r(S–C)/Å	1·819	(0·002)
l(S–C)/Å	0·061	(0·005)
C–C–S	112·0°	(0·9°)
S–C–H	107·0°	(2·2°)
H–C–H	108°	(4°)
C–S–H	90·5°	(3·2°)
τ(S–C–C–S)	106·3°	(3·5°)
n(*anti*) (%)	62	(3)
n(*gauche*) (%)	38	(3)
l(S ⋯ C)	0·074	(0·005)
$l(\mathrm{S} \cdots \mathrm{S})_{gauche}$	0·15	(0·02)
$l(\mathrm{S} \cdots \mathrm{S})_{anti}$	0·122	(0·009)

The experimental radial distribution provided approximate values for the starting structures and the amounts of conformers. Least-squares refinement was carried out by iteration, alternately fixing either the geometrical parameters including mean amplitudes of vibration, or amounts of the two forms, respectively. The refinement was based on the molecular intensities.

Bond lengths, bond angles, torsional angle, some of the mean amplitudes of vibration, and amounts of the two forms (n) determined are presented in the Table. The geometrical parameters do not lead to unexpected conclusions. However, only the values for the S–C bond length and the C–C–S bond angle can be considered really well determined.

The energy difference calculated from the relative abundance of the two conformers is 0·8 kcal mol^{-1}, the *anti*-form being more stable. The vibrational analysis by Hayashi *et al.*[1] yielded 0·6 kcal mol^{-1}, also with the *anti*-form more stable.

A fuller account of this work will soon be submitted to *Acta Chim. Acad. Sci. Hung.*

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† This assumption is supported by the work of Hayashi *et al.*[1]

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