Structure and Rotational Isomerism of Ethylenediamine by Gas Electron Diffraction–Evidence for a Dominant *gauche* Conformer

Akimichi Yokozeki and Kozo Kuchitsu

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

(Received June 16, 1970)

Ethylenediamine is known as a typical chelating agent, and the structures of its complexes have been investigated extensively by X-ray crystallography.[1] However, only a little is known about the structure of free ethylenediamine. Neither the geometrical parameters nor the rotational isomerism have been studied in detail, while the spectroscopic data (IR and Raman) have been only tentatively assigned to a single (*cis*) conformer.[2] The present communication will report on the average structure of ethylenediamine and the rotational isomerism as studied by gas electron diffraction.

Anhydrous ethylenediamine (Guaranteed Reagent) was purchased from the Tokyo Chemical Industry Co., Ltd. Diffraction photographs (q= 7 to 130) were taken at various temperatures between 55°C and 118°C using 40 kV electrons with a high-temperature nozzle[3] and with camera lengths of 114 mm and 249 mm. The experimental and analytical procedures are analogous to those reported elsewhere.[4]

The average structure was determined by a least-squares analysis on the molecular intensity. The hydrogen positions were assumed to be similar to those for methylamine[5] and ethane.[6] The mean amplitudes of vibration were calculated by the use of a plausible force model.[7] The skeleton parameters and their limits of error were found to be: r_g(C–C)$=1.55_6\pm0.01$ Å, r_g(C–N)$=1.468\pm0.005$ Å, and $\angle$C–C–N$=110.2\pm0.8°$. The C–C bond length was about 0.02 Å longer than those in ethane and other *n*-alkanes, whereas the C–N distance was similar to that in methylamine[5] within the limits of error.

The above analysis also gave the average N–C–C–N dihedral angle of $64.0\pm5.0°$, as measured from the *cis* position. Thus, ethylenediamine is dominantly in the "*gauche*" conformation about the C–C axis at the above temperature range. This is also supported by the outstanding peak around 2.85 Å in Fig. 1 (essentially composed of the nonbonded N–N pair), where the experimental radial distribution curve with a damping factor, $\exp(-0.00062\,q^2)$, is compared with the theoretical curves for different conformers. On the other hand, a small peak around 3.8 Å in the experimental curve indicates that a small fraction of the *trans* conformer may also be present.

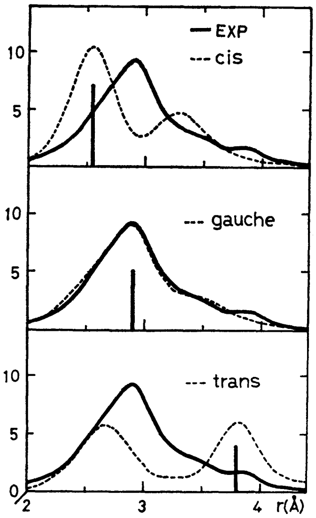

Fig. 1. Radial distribution curves. Solid line: experimental curve, from which the contribution from pairs independent of the internal rotation about the C–C and C–N axes are subtracted to accentuate the comparison. The subtracted peak, 16.4 at 2.5 Å and 1.0 at 2.8 Å, can be reproduced to within 0.2 by a theoretical curve based on the skeleton parameters given in the text with the index of resolution of 100%. The experimental error is estimated to be of the order of 0.4 in the whole region illustrated. Broken lines: corresponding theoretical curves for *cis*, *gauche* and *trans* conformers about the C–C axis with the index of resolution of 100%. Vertical line indicates the nonbonded N–N distance for each conformer.

In the above calculations, the NH_2 group was assumed to have a three-fold potential around the C–N axis with a barrier height of 1.6 kcal/mol, as in the case of ethylamine;[8] a classical average was taken to account for the effect of this motion.[4] The results presented in the preceding paragraphs are, however, found to be essentially independent of the assumptions as to the NH_2 conformation. A further analysis of the internal rotation about the C–C and C–N axes and the geometrical parameters is now being made.

---

[1] For example, M. Iwata, K. Nakatzu and Y. Saito, *Acta Crystallogr.*, **B25**, 2562 (1969).

[2] A. Sabatini and S. Califano, *Spectrochim. Acta*, **16**, 677 (1960).

[3] A. Yokozeki and K. Kuchitsu, to be published.

[4] A. Yokozeki and K. Kuchitsu, This Bulletin, **43**, 2017 (1970).

[5] D. Lide., Jr., *J. Chem. Phys.*, **27**, 343 (1957); H. K. Higginbotham and L. S. Bartell, *ibid.*, **42**, 1131 (1965).

[6] L. S. Bartell and H. K. Higginbotham, *ibid.*, **42**, 851 (1965).

[7] I. Suzuki, This Bulletin, **35**, 1456 (1962).

[8] M. Tsuboi, A. Y. Hirakawa and K. Tamagake, *Nippon Kagaku Zasshi*, **89**, 821 (1968).