experimental points represent mean values at different field strengths without correcting for induced diamagnetism.

The thermomagnetic curve of CrP does not follow the Curie-Weiss Law in any temperature range. Hence, the magnetic susceptibility data are not inconsistent with the absence of cooperative magnetism. The $\chi(T)$ curve of CrP shows a pronounced similarity to that of CrAs [9] above ~ 300 K. (Note that the ordinate axis on Fig. 5 in Ref. 9 represents $\chi_g \times 10^6/\sigma_g \times 10^3$ and not $\chi_g \times 10^4/\sigma_g \times 10^{-4}$ as incorrectly stated in the article.) Thus, a parallel to the helimagnetic structure of CrAs below 261–272 K could be expected. The absence of a helimagnetic structure both for CrP and VAs [15] interrupts the relatively clear trends [13] in the magnetic data for the MnP compounds of the 3*d* transition metals. The "jigsaw puzzle" has to be started all over again based on the inevitable fact that the chemical bonding in these compounds must be discussed in terms of their electronic band structures which appear to depend on the particular combination of elements.

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Ethyleneimine Inversion Barrier and CH_2 Group Twist

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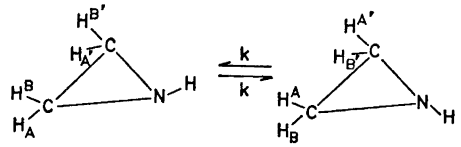
An experimental determination of the barrier to inversion in ethyleneimine has been carried out using the temperature variation of the ^{1}H NMR spectrum of the methylene protons.

The spectra were recorded on a Varian A-60 instrument. The temperature was varied from 5 to 100°C by means of a continuous stream of nitrogen, which was either cooled or heated. The sample consisted of a solution of ethyleneimine in CCl_4 in a molar ratio of 1:2. The solution was thoroughly dried with NaOH as in the study by Bardos *et al.*[1] of 2,2,3,3-tetramethylaziridine. The presence of H_2O leads to rapid intermolecular N–H proton exchange and makes observation of the effects of inversion impossible.

The spectrum of dry ethyleneimine in CCl_4 (Fig. 1) is an AA'BB'X-system, characterized by 3 chemical shifts ν, and 6 coupling constants J.



A: *anti* protons, B: *syn* protons, X: imine proton.

These constants, together with the inversion rate constant k at different temperatures, were determined by comparing experimental spectra with theoretical spectra (Fig. 1) calculated and plotted by a

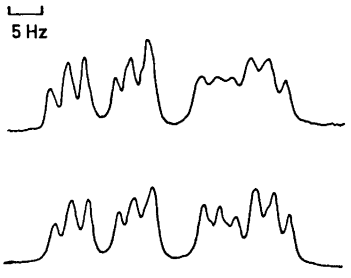


Fig. 1. Methylene part of ethyleneimine spectrum (60 MHz). Upper trace: Experimental spectrum at 5°C. Lower trace: Theoretical spectrum with inversion rate constant $k = 0.0$ sec^{-1}.

programme DNMR3 written by Binsch and Kleier.[2] As starting point, the coupling constants of Mortimer [3] were used. His measurements were performed on a sample with no chemical shift difference between *syn* and *anti* protons (H_2O-catalyzed exchange). His results were, in Herz:

$$J_{AA'} = J_{BB'} = 6.3 \quad J_{AB} = 1.5 \quad J_{AB'} = 3.8$$

The final values found in this work were:

ν_A	$= 0.0$	ν_B	$= -20.5$	ν_X	$= -90.0$
$J_{AA'}$	$= 7.0$	$J_{BB'}$	$= 5.6$	J_{AB}	$= 1.0$
$J_{AB'}$	$= 3.9$	J_{AX}	$= 9.65$	J_{BX}	$= 7.8$

All values are in Herz with uncertainties of about ± 0.1 Herz. The chemical shifts are measured relative to the *anti* protons. The actual chemical shift of the *anti* protons is 294 Herz to the highfield side of benzene (at 60 MHz). The *syn* protons were assumed to be at highest field by analogy with other aziridines.[4]

The values of the inversion rate constant k at different temperatures were fitted to an Arrhenius expression:

$$k = k_0 \exp(-\Delta E/RT)$$

ΔE, the activation energy of inversion, was found from Fig. 2 to be: $\Delta E = 18.8 \pm 0.5$ kcal/mol. A value of 17.3 ± 0.5 kcal/mol for the free energy of activation at the coalescence temperature (68°C) was reported [5] after this investigation had been carried out.

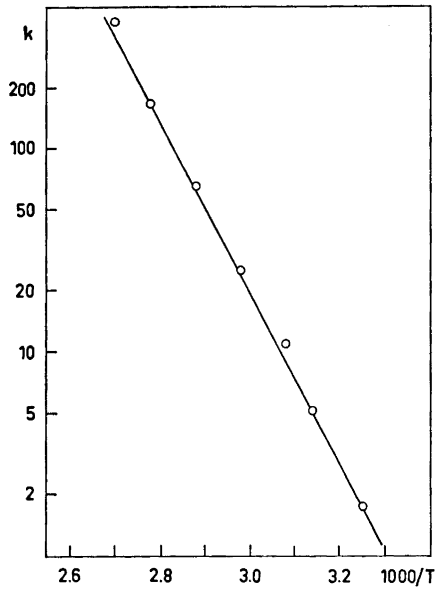


Fig. 2. Inversion rate constant k as a function of $1/T$. T is the temperature in K.

The barrier height found is consistent with a value of 18.3 kcal/mol calculated by Lehn *et al.*[6] employing the *ab initio* method with gaussian functions. A (9,5) basis set contracted to ⟨4,2⟩ was used. The author, using a (7,3) basis set contracted to ⟨4,2⟩ (orbital exponents and contraction coefficients from Roos and Siegbahn [7]), obtained 16.6 kcal/mol.

In the microwave substitution structure,[8] the CH_2 groups are not perpendicular to the N(1)C(2)C(3) plane, but are twisted 3° from perpendicularity. The energy change accompanying the twisting of the CH_2 groups from perpendicularity was calculated in order to investigate, whether the basis set would be able to reproduce the energetic effects of such a minor structural change. The structure found by the microwave method [8] was found to be more stable than a structure with the CH_2 groups perpendicular to the N(1)C(2)C(3) plane by 0.35 kcal/mol, in qualitative agreement with the microwave result.

The inversion energy of *N*-chloroaziridine was also calculated. The calculated barrier height was 26.8 kcal/mol, in agreement with negative NMR-results [9] giving $\Delta E > 21$ kcal/mol.

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