tion preceding breakdown to products, *viz.* protonation of the anilide nitrogen (k_2/k_{-1} = 0.025 for trifluoroacetanilide and 0.0008 for the 2′,6′-dimethyl derivative). The small values of $k_{3,\text{oh}}/k_{-1}$ and $k_{3,\text{HCO}_3}^-/k_{-1}$ also reflect a high degree of steric hindrance in reactions between the tetrahedral intermediate and other species; the value of 1.8 M^{-1} for $k_{3,\text{oh}}/k_{-1}$ is to be compared with 93 M^{-1} for trifluoroacetanilide, and corresponding values for $k_{3,\text{HCO}_3}^-/k_{-1}$ are 1 and 300 M^{-1}. Due to the small value of k_2/k_{-1}, the effect of HCO_3^- on the rate is large despite the small value of the catalytic constant, thus for the lowest curve and highest concentration of HCO_3^- in Fig. 2 the rate is increased more than 600 times.

1. Eriksson, S. O. and Holst, C. *Acta Chem. Scand.* **20** (1966) 1892.
2. Eriksson, S. O. *Acta Pharm. Suecica* **6** (1969) 139.
3. Eriksson, S. O., Meresaar, U. and Wahlberg, U. *Acta Chem. Scand.* **22** (1968) 2773.
4. Eriksson, S. O. and Meresaar, U. *Acta Chem. Scand.* **25** (1971) 2697.
5. Bullock, K. and Grundy, J. *J. Pharm. Pharmacol.* **7** (1955) 755.
6. Pailer, M. and Hubsch, W. J. *Monatsh. Chem.* **97** (1966) 1541.
7. Eriksson, S. O. and Regårdh, C. G. *Acta Pharm. Suecica* **6** (1968) 457.
8. Eriksson, S. O. and Meresaar, U. *Acta Chem. Scand.* **25** (1971) 2688.
9. Eriksson, S. O. *Acta Pharm. Suecica* **6** (1969) 321.
10. Bender, M. L., Ginger, R. D. and Unik, J. P. *J. Am. Chem. Soc.* **80** (1958) 1044.
11. Eriksson, S. O. *Acta Pharm. Suecica* **6** (1969) 121.
12. Gani, V. and Viout, P. *C. R. H. Acad. Sci. Ser. C* **274** (1972) 1746.
13. Schowen, R. L., Jayaraman, H. and Kershner, L. *J. Am. Chem. Soc.* **88** (1966) 3373.
14. Christensson, I. *Acta Chem. Scand.* **18** (1964) 904.

Structural and Magnetic Properties of CrP

KARI SELTE,[a] ARNE KJEKSHUS[a] and ARNE F. ANDRESEN[b]

[a] *Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway and* [b] *Institutt for Atomenergy, Kjeller, Norway*

In view of the interesting cooperative magnetic phenomena which have been disclosed for MnP [1-4] and the isostructural phases FeP,[5] $\text{MnP}_{1-x}\text{As}_x$,[6,7] CrAs,[8-10] $\text{Cr}_{1-t}\text{Mn}_t\text{As}$,[11] MnAs,[12] and FeAs,[13] and the trends in these data, it seemed of interest to explore closer the magnetic properties of CrP. However, the sparse nuclear magnetic resonance and magnetic susceptibility data [14] already at hand indicate that magnetic ordering may be absent in CrP down to 4.2 K. The results of a parallel study on VAs [15] appear to suggest a similar conclusion.

Experimental. Samples were made by heating weighed quantities of the elements (99 % Cr crystal powder and 99.999 % red P from Koch-Light Laboratories) in evacuated, sealed quartz tubes. The samples were maintained for one week at 650°C, crushed, subjected to two further annealings at 850°C with intermediate crushings, and finally cooled to room temperature over a period of three days.

The experimental details concerning the X-ray and neutron diffraction, density, magnetic susceptibility, and diffuse reflectance measurements have been presented in previous communications.[9,13,15]

Results. The composition of the CrP phase, which has no appreciable range of homogeneity, was determined to be $\text{CrP}_{1.00 \pm 0.03}$ by application of the disappearing phase principle to Guinier photographic data. Further support for the stoichiometric 1:1 composition is obtained from the pycnometrically measured density of 5.46 g cm^{-3}.

The results (Table 1) derived by least squares profile refinements of the powder neutron diffraction data taken at 17, 81, and 293 K show that the MnP type crystal structure of CrP remains virtually unchanged below room temperature. In view of the experience gained from our preceding neutron diffraction studies [9,13,15] of isostructural compounds all calculations were

Table 1. Unit cell dimensions and positional parameters for CrP according to space group *Pnma*. (X-Ray diffraction positional parameters are quoted from Rundqvist and Nawapong.[16])

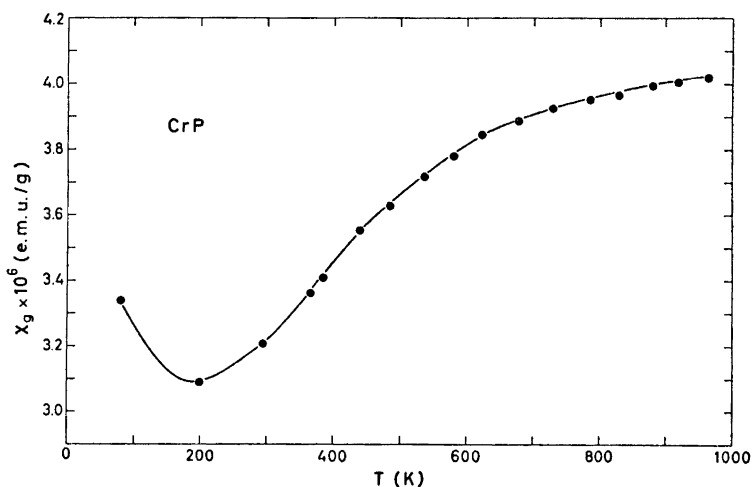| Technique T (K)		Neutron diff. 17	Neutron diff. 81	Neutron diff. 293	X-Ray diff. 293
a (Å)		5.347(2)	5.348(2)	5.356(2)	5.360(2)
b (Å)		3.108(1)	3.109(1)	3.117(1)	3.114(1)
c (Å)		5.996(2)	5.997(2)	6.007(2)	6.018(2)
Cr in 4(c)	x	0.0089(10)	0.0077(11)	0.0074(10)	0.0073(3)
	z	0.1952(8)	0.1942(9)	0.1954(8)	0.1929(2)
P in 4(c)	x	0.1848(7)	0.1856(7)	0.1853(7)	0.1853(5)
	z	0.5641(8)	0.5647(6)	0.5644(6)	0.5653(5)

Fig. 1. Magnetic susceptibility of CrP as a function of temperature.

performed in terms of a model based on space group *Pnma*. In the present case, however, this imposition of constraints in the refinement model is supported by the findings of Rundqvist and Nawapong,[16] who have shown that the room temperature structure of CrP does not deviate significantly from the *Pnma* symmetry. The rather low R-values (ranging between 0.016 and 0.035) obtained by us lend further support to the correctness of *Pnma* in relation to CrP. Except for a minor discrepancy in z_{Cr}, the present values for the positional parameters are in excellent agreement with those found by X-ray diffraction by

Rundqvist and Nawapong [16] (*cf.* Table 1).

The neutron diffraction data show no evidence of cooperative magnetism in CrP above 17 K. A small magnetic contribution to the nuclear reflections is difficult to detect, but we estimate that any possible ordered moment at 17 K must be less than 0.2 B.M.

The magnetic susceptibility *versus* temperature curve for CrP is shown in Fig. 1. The experimental data refer to a single sample, but measurements repeated on other samples confirm the reproducibility of this curve. Field strength dependent susceptibilities were not observed and the

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 $3d$ 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.

1. Felcher, G. P. J. Appl. Phys. 37 (1966) 1056.
2. Forsyth, J. B., Pickart, S. J. and Brown, P. J. Proc. Phys. Soc. 88 (1966) 333.
3. Takeuchi, S. and Motizuki, K. J. Phys. Soc. Japan 24 (1967) 742.
4. Bertaut, E. F. J. Appl. Phys. 40 (1969) 1592.
5. Felcher, G. P., Smith, F. A., Bellavance, D. and Wold, A. Phys. Rev. B 3 (1971) 3046.
6. Ido, H. J. Phys. Soc. Japan 25 (1968) 1543.
7. Hall, E. L., Schwartz, L. H., Felcher, G. P. and Ridgley, D. H. J. Appl. Phys. 41 (1970) 939.
8. Watanabe, H., Kazama, N., Yamaguchi, Y. and Ohashi, M. J. Appl. Phys. 40 (1969) 1128.
9. Selte, K., Kjekshus, A., Jamison, W. E., Andresen, A. F. and Engebretsen, J. E. Acta Chem. Scand. 25 (1971) 1703.
10. Boller, H. and Kallel, A. Solid State Commun. 9 (1971) 1699.
11. Kazama, N. and Watanabe, H. J. Phys. Soc. Japan 30 (1971) 1319.
12. Menyuk, N., Kafalas, J. A., Dwight, K. and Goodenough, J. B. Phys. Rev. 177 (1969) 942.
13. Selte, K., Kjekshus, A. and Andresen, A. F. Acta Chem. Scand. 26 (1972) 3101.
14. Stein, B. F. and Walmsley, R. H. Phys. Rev. 148 (1966) 933.
15. Selte, K., Kjekshus, A. and Andresen, A. F. Acta Chem. Scand. 26 (1972) 4057.
16. Rundqvist, S. and Nawapong, P. C. Acta Chem. Scand. 19 (1965) 1006.

# Ethyleneimine Inversion Barrier and CH₂ Group Twist

STEEN SKAARUP

Chemical Laboratory V, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

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 CCl₄ 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 H₂O leads to rapid intermolecular N−H proton exchange and makes observation of the effects of inversion impossible.

The spectrum of dry ethyleneimine in CCl₄ (Fig. 1) is an AA'BB'X-system, characterized by 3 chemical shifts ν, and 6 coupling constants J.
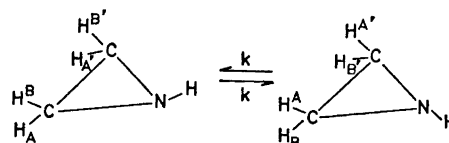
A: anti protons, B: syn protons, X: imine proton.