Crystal Structure and Thermodynamical Investigations of Triethylenediamine, $C_6H_{12}N_2$

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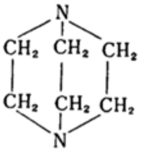
Triethylenediamine, or 1, 4-diazabicyclo-(2, 2, 2)-octane, is considered to be a typical globular cage molecule with high symmetry. In order to amplify our knowledge on the thermal behavior of molecules in crystals, we have studied the crystal structure and some thermodynamical properties of this material.



The sample used for the present research was kindly offered us by Dr. Oae and by Houdry Process Corporation, Pa., U. S. A.

Small single crystals for the X-ray investigation, obtained from a saturated ethereal solution, were kept in glass capillaries to avoid humidity since the material has strong tendency of forming monohydrate. Useful X-ray data were obtained from Weissenberg photographs around *a* and *c* axes respectively taken with Ni-filtered Cu K_α radiation. The crystallographic data are: hexagonal system; $a=6.20\pm0.01$, $c=9.58\pm0.02$ Å; $Z=2$; $D_X=1.17$, $D_{obs}=1.14$ g. cm^{-3} [1]; space group $C_{6h}^2-P6_3/m$.

After seven and six successive calculations of the (F_0-F_c)-syntheses along [001] and [100] respectively, the final atomic parameters (Table I) and temperature factors were obtained. The interatomic distances thus calculated are given in Table II together with their standard deviations. Fig. 1 shows the molecular arrangement in a unit cell projected on (001).

TABLE I. ATOMIC PARAMETERS

	x	*y*	*z*
N	2/3	1/3	0.612
C	0.870	0.571	0.667
H_1	0.024	0.593	0.632
H_2	0.848	0.703	0.632

TABLE II. INTERATOMIC DISTANCES AND BOND ANGLES WITH STANDARD DEVIATIONS (Å UNIT)

C–C	1.590 (0.034)	C–C–N	110°53′
C–N	1.477 (0.017)	C–N–C	108°1′
C–H	0.96		
N···N	2.643 (0.020) (in a molecule)		
	4.276, 6.932 (between molecules)		
C···N	3.748		
C···C	3.876, 3.977		

Molecules are approximately closest packed in the hexagonal lattice. The molecule in crystal has nearly $D_{3h}-\bar{6}m2$. The linkage of N–C–C–N shows a cis configuration. The crystal does not show any disordered structure in the room temperature phase.

In connection with the crystal analysis, differential thermal analysis was carried out up to 180°C. (Fig. 2). The sample, recrystallized from ethereal solution and sublimed repeatedly under high vacuum (10^{-5} mmHg), evacuated sufficiently at an elevated temperature prior to the measurement. The curve shows the presence of a phase transition at 79.8°C**, the entropy change of which is larger than that at the m. p. 161.1°C. These temperatures are more or less higher than those reported hitherto[1]. Measurements of vapor pressures have also been carried out below and above the transition point. The data are summarized in Table III.

The relatively small entropy of fusion shows that the high temperature phase of the crystal might belong to the category of the so-called

TABLE III. VAPOR PRESSURE DATA

Low temperature phase (51.3∼78.6°C)
$\log p(\text{mmHg})=-3233.6_3/T+10.473_2$
$\Delta H=14.8$ kcal./mol.
$\Delta S=34.8$ e. u.
$\Delta G=14.80_6-0.0347_6T$ kcal./mol.

High temperature phase (80.0∼96.3°C)
$\log p(\text{mmHg})=-2722.1_8/T+9.026_9$
$\Delta H=12.5$ kcal./mol.
$\Delta S=28.1$ e. u.
$\Delta G=12.46_4-0.0281_4T$ kcal./mol.

Transition (79.8°C)
$\Delta H=2.3_4$ kcal./mol.
$\Delta S=6.6_2$ e. u.

Fusion (161.1°C)
$\Delta H=1.4_5$ kcal./mol.*
$\Delta S=3.3$ e. u.

* This value was estimated from the differential thermal analysis curve.

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[1] A. Farkas, G. A. Mills, W. E. Erner and J. B. Maerker *J. Chem. Engineering Data*, **4**, 334 (1959).

** According to the private communication from Dr. E. F. Westrum the transition temperature is found to be about 353°K.

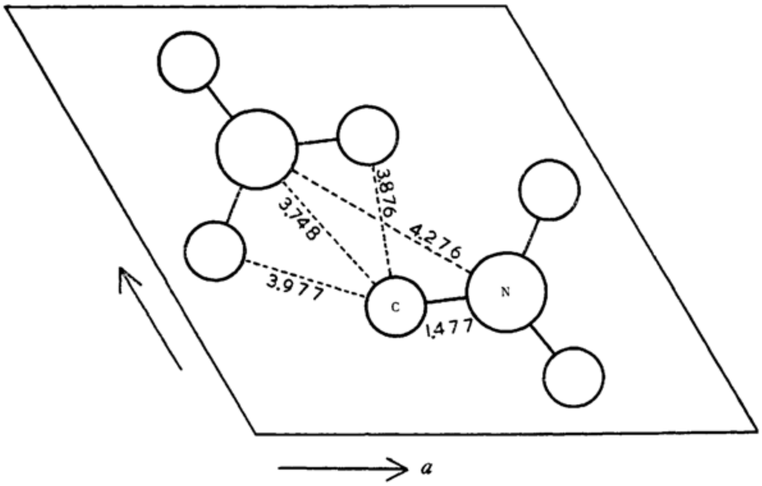

Fig. 1. The molecular arrangement in a unit cell projected on (001).

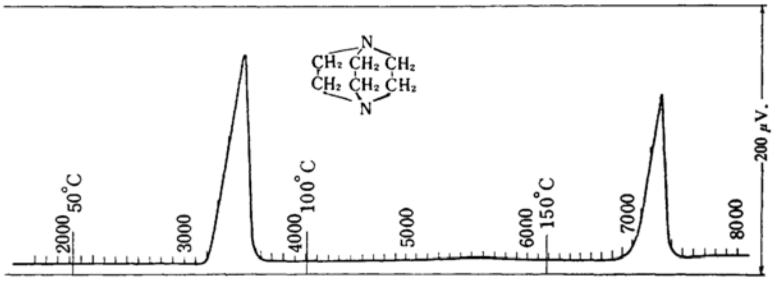

Fig. 2. Automatic recording curve of differential thermal analysis.

"plastic crystals" in the sense as suggested by Timmermans[2]. Accompanied with the large increase of entropy at the transition point, the molecule will gain some orientational, rotational or even translational freedom. Detailed analysis of the crystal structure in the high temperature phase is now going on. The heat capacities near the transition and melting points and the NMR measurement are currently under study in our laboratory. These studies may provide further informations on the mechanism of the phase transition and on the thermal motions in the high temperature phase.

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[2] J. Timmermans, *J. chim. phys.*, **35**, 331 (1938).