

An XRay Study of Symmetrical Trinitrotoluene and Cyclo Trimethylenetrinitramine

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and ours is the fact that from microphotometer records we obtain definite proof that the frequencies 1661 and 1759 cm^{-1} in the spectrum of the crystals have real existence and are as strong as the corresponding frequencies in the aqueous solution. Hibben found that these frequencies were absent in the dihydrate crystals but present in the anhydrous solid. Our results, obtained from crystals which were definitely dihydrate crystals, agree with those of Rao and support our inference regarding the crystals examined by him.

Since Hibben's conclusions that the two carboxyl groups behave differently depend to a large extent on the difference in the spectra of the anhydrous and hydrated crystals we submit that such conclusions may be invalidated by his comparing the spectrum he obtained for his anhydrous crystals with Rao's spectrum for the solid.

To enter into a full discussion of the results is beyond the scope of this letter in which we merely wish to indicate our observations that the Raman spectra obtained from saturated aqueous solutions of oxalic acid and from dihydrated oxalic acid crystals are substantially the same.

W. ROGIE ANGUS
ALAN H. LECKIE

University College,
London, W.C. 1,
December 5, 1935.

¹ Angus, Leckie and Wilson, *Nature* **135**, 913 (1935).

² Hibben, *J. Chem. Phys.* **3**, 675 (1935).

³ Rao, *Zeits. f. Physik* **94**, 536 (1935).

⁴ Krishnamurti, *Ind. J. Phys.* **6**, 309 (1931).

Infrared Evidence for the Existence of an Isomeric Form of HCN

Hydrogen cyanide has been shown by the experiments of Badger and Binder¹ and of Choi and Barker² to be a rectilinear molecule with a simple structure of the vibration-rotation lines. In their work on hydrocyanic gas these investigators found an absorption band with a maximum at 4.76μ .

In recent studies of the effects of isomerism on infrared absorption spectra the writer finds that all organic cyanides have an intense absorption band near 4.5μ , while the isomeric forms of these compounds in which the carbon is divalent give rise to more intense bands at slightly longer wave-lengths. The shift in band position due to isomerism is found to be approximately 0.2μ in every case studied.

The work of Nef³ and his co-workers seems to indicate the existence of a small amount of the isomer HNC in all hydrocyanic gas. A study of the absorption of a saturated solution of hydrocyanic gas in the region between 4.5μ and 5μ reveals a strong band at 4.76μ and a much weaker band at 4.95μ . The absorption at 4.95μ is attributed to the presence of a small amount of the isomer HNC in the solution. From a comparison of intensities it would seem that the isomer HNC makes up about two percent of the gas in aqueous solution.

DUDLEY WILLIAMS

University of North Carolina,
Chapel Hill,
December 5, 1935.

¹ R. M. Badger and J. L. Binder, *Phys. Rev.* **37**, 800 (1931).

² K. N. Choi and E. F. Barker, *Phys. Rev.* **42**, 777 (1932).

³ J. V. Nef, *J. Am. Chem. Soc.* **26**, 1549 (1904).

An X-Ray Study of Symmetrical Trinitrotoluene and Cyclo Trimethylenetrinitramine

An x-ray study of the above crystals was undertaken with the hope of finding the crystal structure of these powerful explosives and thus contribute toward an understanding of why they decompose violently to shocks of a definite frequency while being unaffected by much stronger shocks of a different frequency. Although the crystal structures proved to be too complicated to be readily found, the symmetries of the crystals and their unit cells were determined.

Professor Tenney L. Davis of the Massachusetts Institute of Technology kindly furnished the crystals.

The trinitrotoluene crystals had been obtained by precipitation in benzene. They were amber in color and flattened along the b axis with (210), (110), (011) and (010) prominent.

There are two reports* as to the crystallographic symmetry of symmetrical trinitrotoluene. Friedländer reports it to be orthorhombic with $a : b : c = 0.7586 : 1 : 0.5970$. Artini later reported that he had detected a slight inclination of the c axis and that the crystals were therefore monoclinic.

Our Laue photographs clearly show two planes of symmetry parallel to the b axis. Since the intensity of Laue spots is very sensitive to the symmetry, it may be regarded as established that TNT is really orthorhombic. Complete rotation photographs give $a = 14.85\text{\AA}$, $b = 39.5\text{\AA}$, and $c = 5.96\text{\AA}$ in agreement with the crystallographic ratios. If there are 16 molecules in the unit cell, the calculated density is 1.710, compared with 1.654 given in the literature.

Reflections $hk0$ are missing for either h or k odd and $0kl$ for k odd. However, the latter is a special case of the non-space group vanishing hkl for h even and k odd, which occurs. This can be accounted for by special positions of the molecules, but the intensity calculations are very complicated and were not carried further.

The cyclo trimethylenetrinitramine crystals were transparent with beautifully developed faces and a brilliant luster. Mr. Harry Berman, mineralogist at Harvard, kindly examined them crystallographically for us. He reported them to be orthorhombic with $a : b : c = 0.878 : 1 : 0.819$.

X-ray photographs confirm this. We obtain $a = 11.5\text{\AA}$, $b = 13.2\text{\AA}$, and $c = 10.6\text{\AA}$. With eight molecules in the unit cell, the calculated density is 1.82. Reflections $0kl$ with l odd, $h0l$ with h odd and $hk0$ with k odd are missing. All space groups are eliminated except V_h' , V_h^5 , V_h^{11} , and V_h^{15} with the last most probable since it accounts for all the extinctions.

I am indebted to the Massachusetts Institute of Technology which furnished the facilities for this research and to the National Research Council for the National Research Fellowship under which this work was done.

RALPH HULTGREN

Graduate School of Engineering,
Harvard University,
November 21, 1935.

* Groth, *Chem. Krist.* **4**, 364,766.