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THE STRUCTURE OF 1,2,3-TRIAZINE

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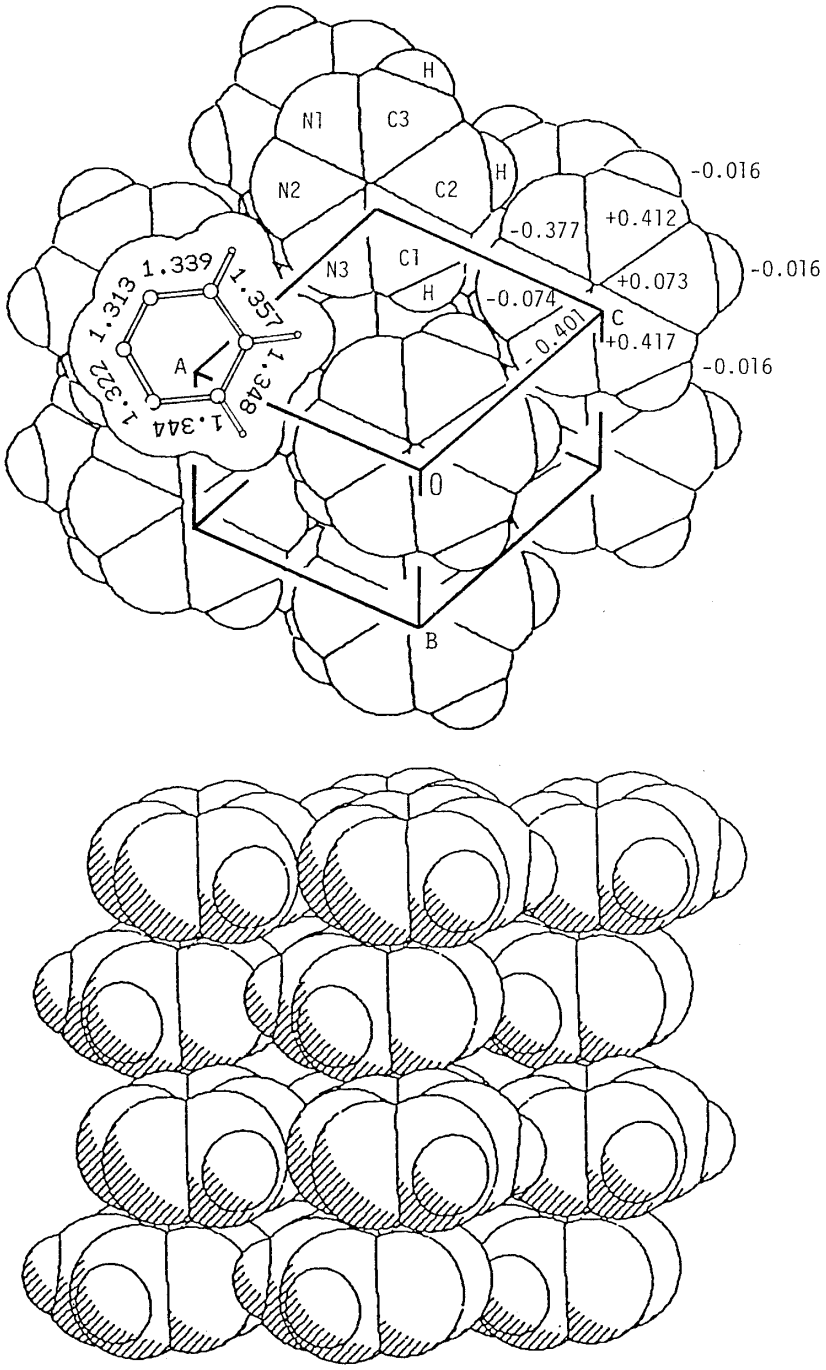
The structure of 1,2,3-triazine was elucidated by X-ray crystallographic analysis, and ab initio SCF-MO calculations were performed for this compound based on the crystallographic coordinates.

KEYWORDS —— X-ray analysis; SCF-MO calculation; 1,2,3-triazine; dipole moment

1,2,3-triazine, one of the basic azabenzenes, is not known to occur in nature; however, the chemistry of its derivatives has attracted considerable interest. Although a number of theoretical calculations have been performed on triazabenzenes including 1,2,3-triazines[1] and several structural investigations have been carried out for modified triazines, detailed structure analyses of unsubstituted pyridazine[2] and triazine have not been reported. This paper describes a successful X-ray diffraction study of 1,2,3-triazine. Although the elucidation of the detailed structure of the compound was expected,[3] an attempted X-ray study failed because of instability of the crystal.[4] However, it has since been shown that the instability was caused by the adhesive used to mount the crystal. We have observed little damage by X-ray irradiation in the present study. In the present work, sublimation of the crystal was prevented by enclosing the crystal in a thin-walled glass capillary. The analysis was performed using a crystal of dimensions 0.45 X 0.32 X 0.25 mm, which grew from dioxane-ether solution as a colorless flake. The lattice constants and intensity data were obtained on a Philips PW1100 diffractometer with graphite-monochromated CuKα radiation using the θ-2θ scan method. The space group of the crystal is triclinic $P\bar{1}$ with two molecules per cell. The cell dimensions are a=6.941(3), b=5.785(3), c=5.751(3) Å, α=112.71(2), β=104.02(2), γ=97.58(2)°. A total of 678 reflexions was measured within the 2θ range of 6° through 156°. The decay in intensities of three different standard reflexions measured every two hours was less than 1% during data collection.

The crystal structure was determined by direct method using MULTAN[5] and refined by the block-diagonal least-squares method using the HBLS IV[6] program. The final R value was 0.059 including refined hydrogen atoms.[7] The bond lengths (Å) and the stacking of this molecule in the crystal (lateral view and a plane figure) are illustrated in the Figure, drawn with the Corey-Pauling-Koltun model by the PLUTO program[8] (Van der Waals radii are assumed to be C=1.6, N=1.4 and H=1.0 Å).



Figure

As shown in the Figure, the N---N bond lengths are 1.313 and 1.322 (Å) and the N---C bond lengths are 1.399 and 1.344 (Å). These values are in good agreement with those found in 4,5,6-tris[p-methoxyphenyl]-1,2,3-triazine.[9]

The C---C bond lengths of 1.348 and 1.357 (Å) are significantly shorter than the normal C---C bond lengths, and are inconsistent with the above compounds. The differences between the bond lengths found in this study and those found in pyridazine hydrochloride[10] are compared with each other. The N---N, N---C and C---C bond lengths in the latter compound are 1.334, 1.314 and 1.377∿1.409 (Å), respectively.

The degree of electron delocalization in the molecule was estimated by ab initio SCF-MO calculations.[11] Net atomic charges (a.u.) are also shown in the Figure. The dipole moment, 6.24(D), calculated by the SCF-MO method is reasonable as compared with values measured for pyridine, 2.19(D), and pyridazine, 3.95(D).[12] The correlation between chemical reactivity and physical properties of the present compound is a subject of continuing studies.

REFERENCES AND NOTES

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7) The atomic co-ordinates for this study are available on request from the Director of the Cambridge Crystallographic Data Center, Cambridge, England. The list of Fo and Fc values may be obtained from on of the authors (K.Y.) upon request.
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