CONFIGURATION OF (Z)-2-IODO-2-PHENYLHYDRAZONOACETONITRILE BY X-RAY DIFFRACTION

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It has been reported¹ that the attempted isomerization of (Z)-2-cyano-2-phenylhydrazonoacetic acid (1) by iodine catalysis in ethanolic solution yielded yellow crystals which had no carbonyl stretching frequencies in the infrared

spectrum. Infrared and chemical evidence supported the conclusion that this product is an isomeric form of the compound 2-iodo-2-phenylhydrazonoacetonitrile (2). The X-ray crystal structure of (2) was undertaken to determine its configuration.

Crystal Data

 $C_8H_6N_3I; M = 271.06;$ orthorhombic, $a = 12.84(1), \dagger b = 14.875(9), c = 4.78(2)$ Å; $U = 913.0; D_m = 1.94$ (by flotation); $D_c = 1.97; Z = 4;$ space group: $Pn2_1a$ $(C_{2v}^9);$ $F(000) = 152; \mu = 277.06$ cm⁻¹ (Cu K α radiation).

Three-dimensional intensities were collected using the equi-inclination Weissenberg technique about the a (0kl-7kl) and c (hk0-hk4) axes, and visually estimated. The data, 740 independent reflections, were corrected for absorption, Lorentz and polarization factors. No overall correction was made for extinction but five reflections appeared to be affected and were given low weights in the final stages of refinement.

The atomic parameters for the iodine atom were determined from an analysis of the interatomic vectors in a three-dimensional F^2 (Patterson) synthesis. A structure factor calculation based on the iodine atom gave a conventional

$$R_1 = [\sum |(|F_{obs}| - |F_{eale}|)| / \sum |F_{obs}|] = 0.189$$

An electron density synthesis using F values with signs based on the iodine coordinates, contained a false mirror plane at y = 1/4, and also a series of concentric ripples about the iodine position. Using a series of Fourier and difference Fourier syntheses, the remaining 11 non-hydrogen atoms were determined, dropping R_1 to 0.156. Three cycles of full matrix least squares refinements reduced R_1 to 0.138. The positional coordinates of the atoms together with their isotropic temperature factors are tabulated in Table 1. Table 2 lists the interatomic distances and compares them

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- † Values in brackets refer to the standard deviation in terms of error in last decimal place.
- ¹ Brecknell, D. J., Carman, R. M., Deeth, H. C., and Kibby, J. J., Aust. J. Chem., 1969, 22, 1915.

Aust. J. Chem., 1970, 23, 395-7

SHORT COMMUNICATIONS

TABLE	1
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Atom	x/a	y/b	z/c	B
I	0.1107(2)	0.2500	0.1652(6)	$3 \cdot 19(6)$
N 1	0.384(4)	0.347(3)	-0.021(14)	$4 \cdot 6(10)$
N2	0.204(3)	$0 \cdot 414(2)$	0.455(8)	$2 \cdot 2(6)$
N3	0.115(3)	$0 \cdot 417(2)$	0.589(8)	$2 \cdot 5(6)$
C 1	0.316(5)	0.349(4)	$0 \cdot 123(13)$	$4 \cdot 2(11)$
C2	0.218(3)	$0 \cdot 352(2)$	0.290(9)	$2 \cdot 1(7)$
C 3	0.094(4)	0.487(3)	0.795(11)	$2 \cdot 8(8)$
C4	0.006(4)	0.486(2)	0.936(9)	$2 \cdot 1(7)$
C 5	-0.005(4)	0.560(3)	$1 \cdot 138(11)$	$3 \cdot 1(8)$
C 6	0.051(6)	0.619(5)	$1 \cdot 229(16)$	$5 \cdot 4(14)$
C7	0.159(5)	0.620(3)	$1 \cdot 051(13)$	$3 \cdot 9(10)$
C 8	0.190(6)	0.547(4)	0.834(14)	$4 \cdot 8(12)$

FRACTIONAL POSITIONAL COORDINATES, AND THERMAL PARAMETERS (\hat{A}^2) Estimated standard deviations are reported in brackets. These values are

TABLE 2

INTERATOMIC DISTANCES d (Å)

Estimated standard deviations in brackets. Since the scatter in the aromatic ring interatomic distances is as much as 0.2 Å, the values of 0.08 Å seem underestimated. d', Values for similar bonds in phenylhydrazine

Bond	d	Bond	d	d'	Bond	d	d'
I-C 2 N 1-C 1	$2 \cdot 14(4)$ $1 \cdot 11(5)$	N 2–N 3 N 3–C 3	$1 \cdot 31(6) \\ 1 \cdot 46(6)$	$1 \cdot 46(4)$ $1 \cdot 42(3)$	C 5C 6 C 6C 7	$1 \cdot 22(8)$ $1 \cdot 63(8)$	$1 \cdot 45(4)$ $1 \cdot 38(3)$
C 1–C 2 C 2–N 2	$1 \cdot 50(6) \\ 1 \cdot 22(6)$	C 3–C 4 C 4–C 5	$1 \cdot 33(8) \\ 1 \cdot 47(8)$	$1 \cdot 40(3) \\ 1 \cdot 46(4)$	C 7–C 8 C 8–C 3	$1 \cdot 56(8) \\ 1 \cdot 52(8)$	$1 \cdot 45(4)$ $1 \cdot 45(4)$



Fig. 1.—Packing of (Z)-2-iodo-2phenylhydrazonoacetonitrile molecules in a unit cell.

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with the values found for phenylhydrazine.² Because of the quality of data collected, refinement was stopped at the isotropic least squares stage. However, the structure analysis has shown that the configuration for the molecule is (Z).

The packing of the unit cell is shown in Figure 1.

Acknowledgments

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² Srinivasan, S., and Swaminathan, S., Z. Kristallogr. Kristallgeom., 1968, 127, 442.