Single Crystal X-Ray Structure Determinations of the Reaction Products of *cis*- and *trans*-Cyclohexanedicarboxylic Anhydrides and Methylhydrazine

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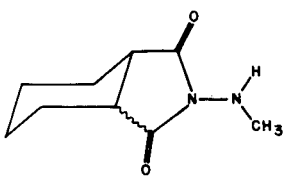
The structures of two of the three isomeric products of the reactions between *cis*- and *trans*-cyclohexanedicarboxylic anhydrides and methylhydrazine were determined by single-crystal X-ray methods to ascertain their tautomeric forms and stereochemistries. One product was found to be *cis*-*N*-methylamino-1,2-cyclohexanedicarboxoimide and the other *trans*-hexahydro-2-methylcyclohexa[*d*]pyridazine-1,2-dione.

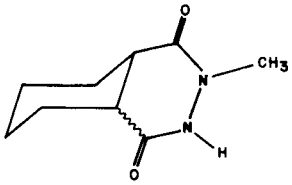
J. Heterocyclic Chem., 13, 931 (1976).

Sir:

At room temperature both *cis*- and *trans*-cyclohexanedicarboxylic anhydrides react with methylhydrazine to give the same product identified as *N*-methylamino-1,2-cyclohexanedicarboxoimide (**1**) on the basis of mass, nmr and ir spectra ($\tilde{\nu}$ = 1770 and 1690 cm^{-1}, characteristic of a cyclic 5-membered imide carbonyl). However, the configuration of **1** could not be deduced. The same reactants, heated under reflux gave mixtures of two products, **2** and **3**, which were separated and characterized as hexahydro-2-methylcyclohexa[*d*]pyridazine-1,4-diones ($\tilde{\nu}$ = 1650 cm^{-1}, m.p. = 171-172° and $\tilde{\nu}$ = 1660 cm^{-1}, m.p. = 226-227°, respectively), again without configurational elucidation (compounds **1**, **2** and **3** all have the same empirical formula). Furthermore, it was not known whether the compounds existed as the enol or keto tautomers. To establish the stereochemistries, X-ray crystal structure determinations of **1** and **3** were undertaken (suitable crystals of **2** could not be grown).



1



2 & 3

Intensity data were measured at -40° by the ω-scan technique in the range $4° < 2\theta < 55°$ using a Syntex $P2_1$ diffractometer with Mo Kα (λ = 0.71069 Å) radiation monochromatized by a graphite crystal. Both structures were solved by the symbolic addition method and refined by full-matrix least-squares.

Table 1

	1	3
a	11.618(1) Å	6.0217(5) Å
b	6.4645(6)	7.8687(7)
c	13.296(1)	19.100(2)
β	113.664(6)°	102.04(1)°
Volume	914.64 Å^3	885.09 Å^3
No. of molecules/-unit cell	4	4
Space group	$P2_1/c$	$P2_1/c$
Scan speeds	1-5°/min	1-4°/min
No. of reflections, measured	2100	2030
No. of reflections, observed	1784 > 2σ(I)	1526 > 2σ(I)
R	0.038	0.038
R_{wtd}	0.043	0.045

Figures 1(a) and (b) give the bond distances and angles, respectively, of **1**, verifying the structural assignment based upon spectral data. The interesting feature of **1** is the *cis*-conformation obtained even when the starting anhydride was *trans*-. No hydrogen bonding was observed.

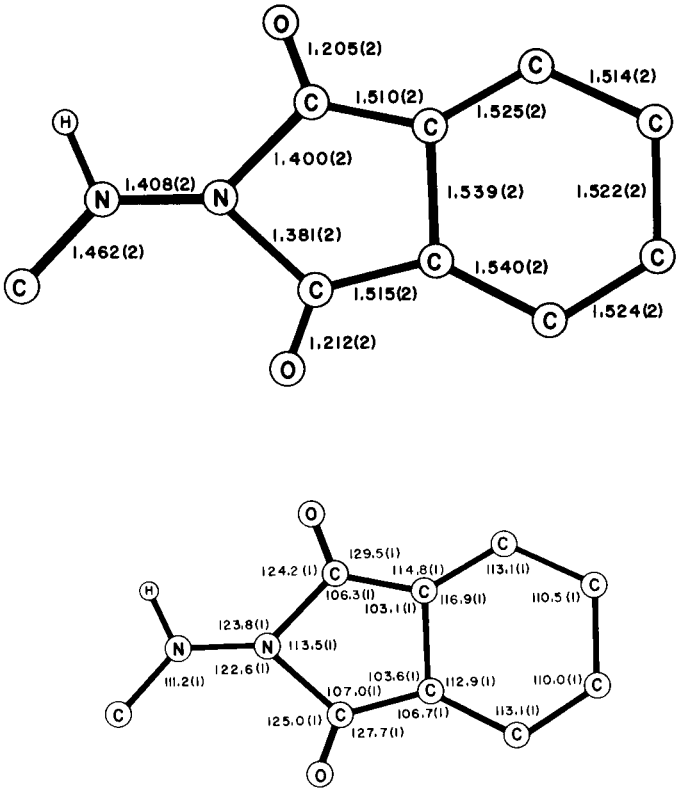


Fig. 1. *cis*-*N*-Methylamino-1,2-cyclohexanedicarboximide (a) Bond lengths (Ångstroms); (b) Bond angles (°).

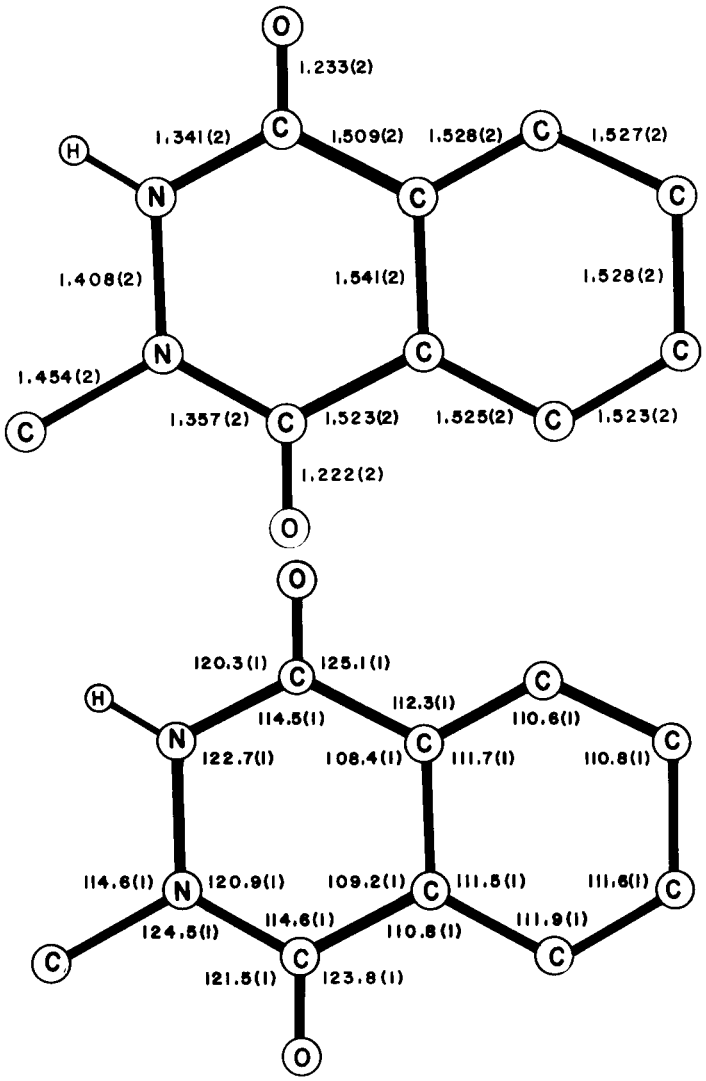


Fig. 2. *trans*-Hexahydro-2-methylcyclohexa[*d*]pyridazine-1,4-dione
(a) Bond lengths (Ångstroms); (b) Bond angles (°).

The structure of **3** is in agreement with the assigned structure; the configuration is *trans*-, therefore **2** should be *cis*-. The keto tautomer is present in the solid state. There is an intermolecular hydrogen bond between the oxygen of the carbonyl adjacent to NH and the nitrogen of another molecule related by a 2-fold screw axis, forming an infinite polymeric chain in the crystal. The N · · · O distance is 2.823(2) Å and the N-H · · · O angle is 163(2)°. Bond distances and angles are given in Figures 2(a) and (b), respectively.

In both **1** and **3** the cyclohexane rings are in the chair conformation.

Acknowledgement.

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