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PREPARATION AND STRUCTURE OF DIMETHYL 1,2-DICYANO-1a, 2b, 2, 7b-TETRAHYDRO-1*H*-AZIRINO[1,2-*a*]CYCLOPROPA[*c*]QUINOLINE-1,2-DICARBOXYLATES

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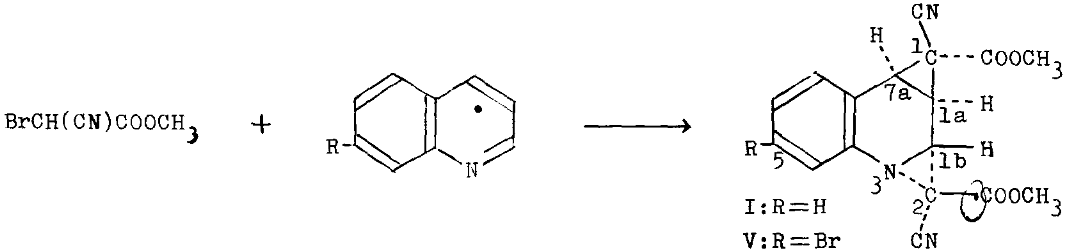
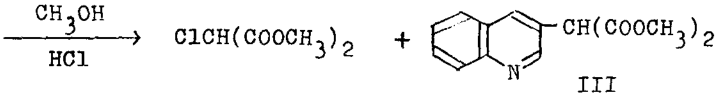
We wish to report that dimethyl 1,2-dicyano-1a, 1b, 2, 7b-tetrahydro-1*H*-azirino[1,2-*a*]cyclopropa[*c*]quinoline-1,2-dicarboxylate (I) with an unknown ring system was produced, when quinoline was used in the process of the investigation (1) to obtain the corresponding ylides from heteroaromatic amines and methyl bromocyanoacetate.

After methyl bromocyanoacetate and quinoline (2-5 mole eq.) were allowed to stand in methanol for one day at room temperature, I was precipitated in 60-66% yield. Recrystallization from a mixture of methanol and acetone gave colorless prisms. The compound turned brown at about 180° and gradually decomposed at about 200°, showing no constant melting point.

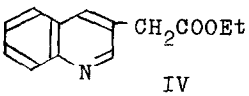


The structure of I was estimated from the following facts. From the result of elemental analysis, I was found to be $C_{17}H_{13}O_4N_3$. NMR spectrum (in DMSO-d_6, TMS as internal reference) showed the signals of 7.65-7.25δ (4H, multiplet, aromatic protons), 3.83 and 3.80 δ (3H each, singlet, $COOCH_3$), 3.78 δ (1H, singlet, C_{1b}-H), 3.36 and 3.12 δ (1H each, doublet (J = 8.7 Hz), C_{7b}-H and C_{1a}-H). This rather high value of the protons on cyclopropane ring is caused by the combined deshielding effects of the cyano and ester groups (2). It is presumed from the absence of the spin-spin coupling between C_{1a}-H and C_{1b}-H on the strained rings that these two hydrogen atoms have the trans configuration (3). IR spectrum (KBr disk) showed absorption bands at 2241 ($\nu_{C\equiv N}$), 1760, and 1744 cm^{-1} ($\nu_{C=O}$). UV spectrum did not show distinct absorption maxima but an end absorption curve with a little shoulder at about 250 mμ (ε=6650).

When allowed to stand over night at 0° in anhydrous methanol saturated with hydrogen chloride, I produced dimethyl chloromalonate (II) (4) and dimethyl 3-quinolinemalonate (III), mp 87-88°. III was identified by deriving it into ethyl 3-quinolineacetate (IV) (5).



III



IV

Since it is difficult to determine chemically the full configuration of I, 5-bromo derivative (V) was prepared for X-ray diffraction analysis by the heavy atom method. V, like I, gradually decomposed at about 200° and showed no constant melting point. The fact that NMR spectrum of V, besides showing the absorption of three aromatic protons, was similar to that of I shows no difference between the configurations of I and V.

X-ray study------ The crystals of V were grown from the mixture of acetone and methanol solutions as orthorhombic colorless, transparent plates elongated along the a-axis. These crystals belong to the orthorhombic system, space group $Pna2_1$ with the lattice constants, a = 8.21, b = 17.77, and c = 11.20 Å, which were determined from hk0 and h0ℓ precession photographs using CuKα radiation. The unit cell contains four molecules if the density of the crystal is assumed to be 1.59 g.cm^{-3}.

Three dimensional intensity data were collected from the equi-inclination Weissenberg photographs. The layers 0hl-4kl about the a-axis were taken with CuKα radiation using the multiple-film technique. The intensities were estimated visually with the aid of calibrated intensity scale to give a total of 706 independent non-zero observed structure factors.

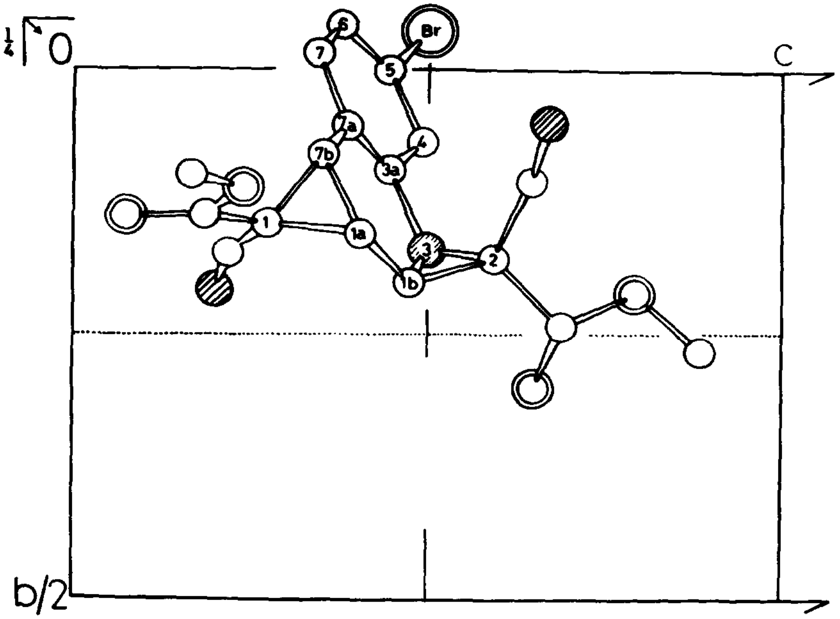


Fig. 1. Projection of the crystal structure along the a-axis. Only one molecule is shown. Single circles indicate carbon atoms, partly shaded circles, nitrogen atoms and double circles, oxygen atoms.

The crystal structure was solved by the heavy atom method and refined by the block-matrix least-squares method. Since the bromine atoms lie nearly on the n- and a- glide planes, the Fourier map phased by the bromine atoms showed pseudo-mirror planes at $x = \frac{1}{4}$ and $z = \frac{1}{2}$. These pseudo-mirror planes could be eliminated by assigning the atoms of one of the quinoline rings to the phasing atoms. Five cycles of the block-matrix least-squares calculations with isotropic thermal parameters reduced the R factor to 0.18. The inter-layer scale factors were adjusted by correlating the observed and calculated structure factors on various layers. Further refinement was carried out by the block-matrix least-squares calculations including the individual anisotropic thermal parameters for each atom. The R factor is now 0.12. Fig. 1 is the a-axis projection of the crystal structure showing one of the molecules by perspective drawing.

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