The Crystal and Molecular Structure of 2-Acetoxy-2-methyl[1,3]dioxolo-[4,5-*c*]isoquinoline-5-carbonitrile. A Photoproduct of 1,4-Diacetoxy-2,3-diazidonaphthalene

Yukishige KITANO,* Tamaichi ASHIDA,** and Akira YABE***

Toray Research Center, Inc., Sonoyama, Ohtsu 520

***Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464*

****National Chemical Laboratory for Industry, Yatabe-Higashi 1-1, Tsukuba, Ibaraki 305*

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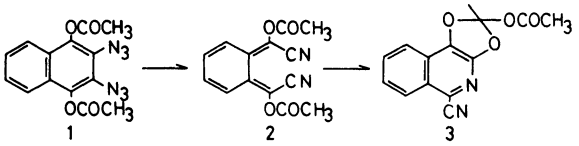
Synopsis. The crystal of the title compound is triclinic, with a space group of $P\bar{1}$ and with two molecules per unit cell with dimensions of $a=8.317$ (2), $b=11.191$ (1), $c=7.731$ (1)Å, $\alpha=105.91$ (1), $\beta=103.76$ (2), and $\gamma=102.60$ (1)°. The fused isoquinoline and dioxolane rings lie on nearly the same plane; the non-hydrogen atoms of the acetoxyl and methyl groups make another plane. These two planes make an angle of 92.0° with each other.

In a series of photolyses of organic azides, it has been reported that 1,4-diacetoxy-2,3-diazidonaphthalene (**1**) gave efficiently an unexpected photoproduct (**3**) *via* α,α′-dicyano-*o*-quinodimethan (**2**) by prolonged photo-irradiation at 77 K in a rigid medium.[1] The structure



of the product was studied spectroscopically, but could not be established exclusively. The compound, obtained in the form of single crystals, was then submitted to X-ray analysis.

Experimental

Single crystals of the compound were grown by the slow evaporation of an ethanol–dichloromethane solution at room temperature. They were yellow plates tabular on (100), elongated in the *c* direction. The lattice constants were obtained by a least-squares fit of 2θ values of 15 reflections measured on a Rigaku automated four-circle diffractometer.

Crystal Data. $C_{14}H_{10}H_2O_4$, MW=270.24, Mp=146 °C (dec), triclinic, $P\bar{1}$, $a=8.137$ (2), $b=11.191$ (1), $c=7.731$ (1)Å, $\alpha=105.91$ (1), $\beta=103.76$ (2), $\gamma=102.60$ (1)°, $V=640.5$ Å^3, $Z=2$, $d_{obsd}=1.41$, $d_{calcd}=1.402$ g cm^{-3}, μ (for Cu $K\alpha$)=8.95 cm^{-1}.

The intensity data were collected from a crystal having dimensions of $0.3\times0.4\times0.3$ mm. The intensities were recorded in the 2θ-ω scan mode with a speed of 10° (ω) min^{-1} and the range of $(1.0+0.142\tan\theta)$° (ω), graphite-monochromated Cu $K\alpha$ radiation being used. 2270 independent reflections with $2\theta\leq135$° were obtained, of which 2208 were non-zero reflections. The intensities of three reference reflections, periodically remeasured, decreased gradually during data collection. The intensity data were corrected for crystal deterioration and for Lorentz and polarization effects, but no absorption correction was applied.

Structure Determination and Refinement

The structure was solved by the direct method with the MULTAN 78 program,[2] refined by the block-diadonal least-squares procedure with the HBLS V program.[3] In the refinement, the function minimized was $\sum\omega(|F_o|-|F_c|)^2$ with the weight scheme of $\omega=k$ for $F_o=0$, and $\omega=(\sigma^2(F_o)+a|F_o|+b|F_o|^2)^{-1}$ for $F_o\neq0$, where $\sigma(F_o)$ is the standard deviation based on the counting statistics. The final refinement ($k=7.28$, $a=-0.666$, and $b=0.025$) led to the *R*-index ($\sum||F_o|-|F_c||/\sum|F_o|$) of 0.0624 for all the reflections and 0.0610 for the non-zero reflections. The scattering factors were taken from the International Tables for X-Ray Crystallography.[4] The final atomic parameters for the non-hydrogen atoms are given in Table 1.[5]

Table 1. Positional($\times10^4$) and thermal ($\times10^2$) parameters for the non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}/Å^2 a)
C(1)	5267(3)	2399(2)	8348(3)	302
C(2)	3943(3)	1337(2)	8180(3)	309
C(3)	2337(3)	1370(3)	8465(4)	384
C(4)	1142(4)	244(3)	8238(4)	448
C(5)	1526(4)	−957(3)	7767(4)	449
C(6)	3037(4)	−1017(2)	7494(4)	393
C(7)	4326(3)	123(2)	7672(3)	320
C(8)	5931(3)	125(2)	7374(3)	326
C(9)	6768(3)	2268(2)	8044(4)	328
C(10)	6931(3)	4387(2)	8734(4)	344
C(11)	6310(4)	−1100(3)	6796(4)	400
C(12)	8237(3)	5041(3)	12101(4)	381
C(13)	9078(4)	6240(3)	13831(4)	456
C(14)	6663(4)	5070(3)	7300(4)	492
N(1)	7185(3)	1188(2)	7557(3)	353
N(2)	6584(4)	−2069(2)	6333(4)	573
O(1)	5281(2)	3675(2)	8773(3)	337
O(2)	7846(2)	3460(2)	8267(3)	381
O(3)	7876(2)	5351(2)	10515(2)	324
O(4)	7906(3)	3945(2)	12105(3)	569

a) The equivalent isotropic temperature factor defined by W. C. Hamilton (*Acta Crystallogr.*, **12**, 609 (1959)).

Results and Discussion

The bond lengths and angles are shown in Fig. 1, together with the atomic symbols.

All the atoms of the fused heterocyclic ring lie on the same plane; the average deviation of the thirteen ring atoms from the plane is 0.008 Å, with the maximum deviation of 0.017 Å for C(8). The C(11) and N(2) atoms of the cyano group deviate from this plane by 0.069 and 0.118 Å respectively. The non-hydrogen atoms of the acetoxyl and methyl groups bonded to the dioxolane ring also make a plane; the average displace-

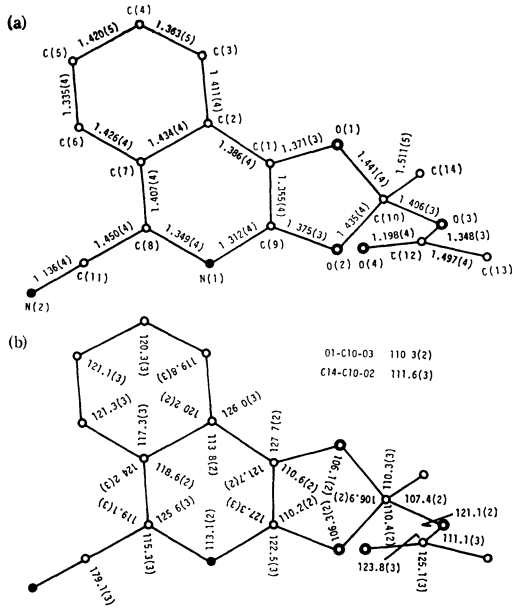


Fig. 1. a) Bond lengths (l/Å) and b) bond angles (ϕ/°) of the compound.

ment of the atoms from the mean plane is 0.030 Å, with the maximum deviation of 0.059 Å for C(13). These two mean planes make an angle of 92.0° with each other.

All the bond lengths and angles are normal. The O(1)–C(10) and O(2)–C(10) bond lengths in the dioxolane ring are in good agreement with the accepted value for the C–O single bond[6] and can well be compared with the corresponding values for the isolated dioxolane ring in 4′-methylsulfonylspiro[1,3-dioxolane-2,4′-piperidine].[7] The somewhat short O(1)–C(1) and O(2)–C(9) lengths can be explained partly in terms of the conjugation of the dioxolane oxygen atoms with the isoquinoline nucleus.

The arrangement of the molecules in the crystals is shown in Fig. 2. The fused heterocyclic rings, approximately parallel to (001), are stacked at intervals of

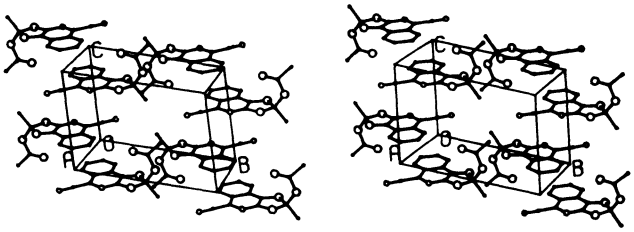


Fig. 2. The arrangement of the molecules in the crystal drawn by the plotter program PLUTO.[8]

3.5 Å along the c axis. The cyano groups of the two molecules around a center of symmetry are antiparallel to each other, leading to favourable dipole-dipole interaction. There are no abnormally short intermolecular contacts.

References

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