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X-Ray Crystal Structures of 2,4-Dimethyl-4,4a-dihydro-1*H*-[1,3,5]triazino[1,2-*a*]quinoline-1,3,6(2*H*,5*H*)-trione and Its Dehydrogenated Derivative. Bond Length and EI Mass Fragmentation

Masami Sawada,* Takanori Tanaka, Yoshio Takai, Yoshiro Furukawa,
Terukiyo Hanafusa, and Soichi Misumi
Material Analysis Center, The Institute of Scientific and Industrial Research, Osaka University,
8-1, Mihogaoka, Ibaraki, Osaka 567
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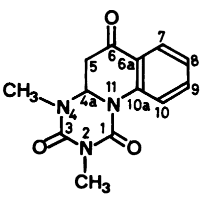
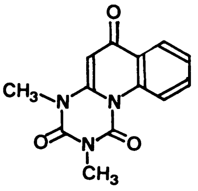
Synopsis. The crystal structures of the cyclic adduct **1** of 4-quinolinone with methyl isocyanate and its dehydrogenated derivative **2** have been determined by X-ray crystal structure analysis. Both crystal structure data of the C–N bond lengths in the triazinedione-ring skeleton suggest which bonds are broken in the initial EI mass fragmentation followed by the subsequent loss of a neutral MeNCO moiety.

Reactions and reactivities of pyridine derivatives have received continuous interest from organic chemists.[1] We recently reported on the preparation of some fused ring 1,3-dialkyl-1,3,5-triazine-2,4-(1*H*,3*H*)-dione derivatives and their mechanisms for the reactions of 4-pyridinone or 4-pyrimidinone with various alkyl isocyanates.[2] Here, we describe the X-ray structures of the parent cyclic adduct, 2,4-dimethyl-4,4a-dihydro-1*H*-[1,3,5]triazino[1,2-*a*]quinoline-1,3,6(2*H*,5*H*)-trione (**1**) and the corresponding dehydrogenated compound (**2**). The crystal structure data may allow to estimate the C–N bond which is broken in the initial EI mass fragmentation followed by the subsequent loss of a neutral molecule.[3]



1



2

Experimental

Colorless crystals of **1** and **2** were obtained by ordinary recrystallization procedures from a hexane/$CHCl_3$ solution and an acetonitrile solution, respectively.[2,3] A single crystal was selected or cut to an appropriate size for each X-ray study. Crystal data and experimental conditions for both **1** and **2** are summarized in Table 1. For the measurements of the unit-cell dimensions and integrated intensities at room temperature, a Rigaku computer-controlled four-circle diffractometer was employed with graphite-monochromatized Mo $K\alpha$ radiation (a rotating anode type, 60 KV, 200 mA; AFC 5FOS). The cell constants were determined by the least squares method from 10—12 reflections. Three standard reflections were checked every 55 reflections during the course of the intensity-data collection and no intensity decrease was observed. The intensities were corrected for the usual Lorentz and polarization effects.

The crystal structures were solved by the direct method with the MULTAN 78 program.[4] The refinements of the structures were performed by the block-diagonal least squares method using the HBLS-V program.[5] Several cycles of refinement, including anisotropic temperature factors and all the hydrogen atoms, reduced the *R* values for both cases (Table 1): the hydrogen atoms of the molecules were found from the difference Fourier maps and

Table 1. Crystal and Experimental Data

Compound	1	2
Formula	$C_{13}H_{13}N_3O_3$	$C_{13}H_{11}N_3O_3$
Molecular Weight	259.16	257.16
Crystal System	Monoclinic	Orthorhombic
Space Group	$P2_1/c$	$P2_12_12_1$
Lattice Constants		
a	14.411(2) Å	14.850(5) Å
b	7.593(3)	10.618(3)
c	10.709(3)	7.066(3)
β	96.34(3)°	
V	1164.6(7) Å^3	1114.2(5) Å^3
Z	4	4
D_c	1.479 gcm^{-3}	1.534 gcm^{-3}
μ(Mo $K\alpha$)	1.164 cm^{-1}	1.212 cm^{-1}
Crystal Size	0.3×0.3×0.25 mm	0.4×0.3×0.25 mm
Scan Method	θ—2θ	θ—2θ
Scan Range $\Delta(2\theta)$	2.0°+0.70°tan θ	2.0°+0.70°tan θ
Scan Speed in 2θ	16°/min	16°/min
$2\theta_{max}$(Mo $K\alpha$)	55°	55°
Background	2×5.5 s	2×2.0 s
No. of Reflections		
Measured	4715	4550
Independent	2681	1531
Used for refinement[a]	2233	1233
R_{sym}[b]	0.016	0.048
Final R	0.0426	0.0612
Final R_w	0.0759	0.0758
a[c]	0.01615	−0.08771
b[c]	0.00039	0.00577

a) $F_o > 3\sigma(F_o)$. b) $R_{sym} = \Sigma(|F_o| - \langle|F_o|\rangle)/\Sigma\langle|F_o|\rangle$. $\langle|F_o|\rangle$: averaged values for symmetry-equivalent reflections. c) See Text.

Table 2. Atomic Positional and Thermal Parameters for **1**[a)]

Atom	x	y	z	$B_{eq}/\text{Å}^2$ [b)]
C(1)	0.6598(16)	0.5358(18)	0.7175(16)	2.56
C(2)	0.624(2)	0.625(3)	0.5009(19)	3.48
C(3)	0.7771(17)	0.4967(19)	0.5692(16)	2.84
C(4)	0.929(3)	0.377(3)	0.639(3)	4.72
C(4A)	0.8220(16)	0.4422(18)	0.7956(16)	2.63
C(5)	0.8767(18)	0.586(3)	0.8694(19)	3.30
C(6)	0.8587(19)	0.5817(19)	1.0054(18)	3.06
C(6A)	0.7691(17)	0.5036(18)	1.0322(16)	2.74
C(7)	0.749(3)	0.488(2)	1.1567(18)	3.40
C(8)	0.665(3)	0.424(3)	1.1834(18)	3.72
C(9)	0.599(3)	0.371(3)	1.0868(19)	3.49
C(10)	0.6169(18)	0.3814(19)	0.9625(17)	2.98
C(10A)	0.7017(17)	0.4497(17)	0.9351(16)	2.47
N(2)	0.6913(14)	0.5551(15)	0.6011(13)	2.71
N(4)	0.8374(15)	0.4376(17)	0.6650(14)	3.06
N(11)	0.7228(14)	0.4635(15)	0.8090(13)	2.55
O(1)	0.5814(13)	0.5782(16)	0.7356(14)	3.82
O(3)	0.7950(15)	0.4993(18)	0.4609(13)	4.32
O(6)	0.9147(16)	0.6400(17)	1.0878(15)	4.50

a) Standard deviations in parentheses refer to the least significant digits. b) Equivalent isotopic temperature factors.[11)]

Table 3. Atomic Positional and Thermal Parameters for **2**[a)]

Atom	x	y	z	$B_{eq}/\text{Å}^2$ [b)]
C(1)	0.224(5)	0.184(4)	0.829(5)	3.04
C(2)	0.269(6)	0.401(5)	0.811(7)	5.47
C(3)	0.382(5)	0.240(4)	0.870(5)	3.00
C(4)	0.496(4)	0.078(5)	0.909(6)	3.92
C(4A)	0.338(4)	0.020(4)	0.864(4)	2.28
C(5)	0.362(4)	−0.102(4)	0.843(5)	3.00
C(6)	0.298(5)	−0.201(4)	0.820(6)	3.36
C(6A)	0.203(4)	−0.163(4)	0.843(5)	2.70
C(7)	0.137(5)	−0.257(5)	0.845(5)	3.64
C(8)	0.049(5)	−0.227(5)	0.875(5)	4.18
C(9)	0.026(5)	−0.104(6)	0.911(6)	4.16
C(10)	0.089(4)	−0.009(5)	0.910(5)	3.36
C(10A)	0.179(4)	−0.038(4)	0.870(4)	2.39
N(11)	0.247(3)	0.057(3)	0.864(4)	2.32
N(4)	0.293(4)	0.268(4)	0.841(4)	3.28
N(2)	0.401(3)	0.114(4)	0.885(4)	2.88
O(1)	0.149(3)	0.217(3)	0.791(5)	4.89
O(3)	0.439(4)	0.320(3)	0.884(4)	4.46
O(6)	0.319(4)	−0.310(4)	0.788(5)	5.87

a) Standard deviations in parentheses refer to the least significant digits. b) Equivalent isotopic temperature factors.[11)]

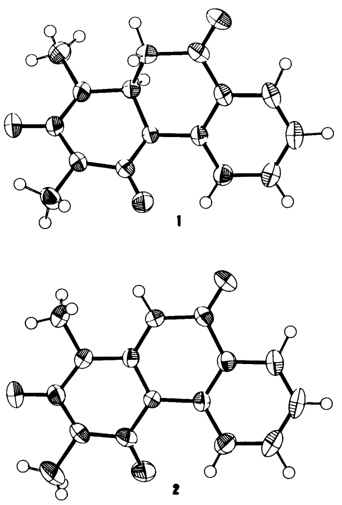


Fig. 1. ORTEP views of the compound **1** and **2**. The nonhydrogen atoms were drawn at the 50% probability level and the hydrogen atoms at an arbitrary diameter.

they were refined with isotropic thermal parameters. The function minimized was $\sum w\,(|F_o|-|F_c|)^2$ with the following weighting scheme: $\omega=1/(\sigma^2(F_o)+a|F_o|+b|F_o|^2)$ for $|F_o|>0$ and $w=0$ for $|F_o|=0$. All the atomic scattering factors of C, N, O were taken from the "International Tables for X-Ray Crystallography".[6)] The computations were carried out on an ACOS-850 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. The final atomic positional and thermal parameters of **1** and **2** are listed in Tables 2 and 3, respectively. The tables of F_o and F_c, and anisotropic thermal parameters of the non-hydrogen atoms are deposited at the Chemical Society of Japan (Document No. 8620).

Results and Discussion

Figure 1 is a computer generated perspective (ORTEP)[7)] view of these structures. The structures which had been previously determined by NMR and other spectral correlations[2)] were confirmed. The bond lengths and the bond angles are given in Fig. 2 and Fig. 3, respectively, together with the atomic numberings. Neither abnormal bond lengths nor bond angles were found in these structures.

EI mass fragmentations of the compound **1** and **2** are reported,[3)] where it is considered that the initial fragmentation of **1** mainly proceeds to the loss of a neutral MeNCO dimer via C(4A)–N(4) bond cleavage, yielding the *M/Z* 145 ion, and that of **2** proceeds to the loss of a neutral MeNCO monomer via C(1)–N(11) cleavage, yielding the *M/Z* 200 ion (Fig. 4).

In the present triazinedione ring, there are five C–N bonds directly concerned with the possible cleavage which is followed by the subsequent loss of the neutral molecule: i.e., C(4A)–N(4)–C(3)–N(2)–C(1)–N(11). The crystal data of the bond lengths in Fig. 2 show that the C(1)–N(11) bond for **2** is the longest among the five C(sp^2)–N bonds: on the other hand, the C(4A)–N(4) bond for **1** is the longest because of the C(sp^3)–N constituent. Therefore, although the comparison is restricted, the longest C–N bond among the five bonds seems to identify the C–N bond to be broken in the initial EI mass fragmentation giving the subsequent loss of the neutral nMeNCO moiety (n=1 or 2). A similar

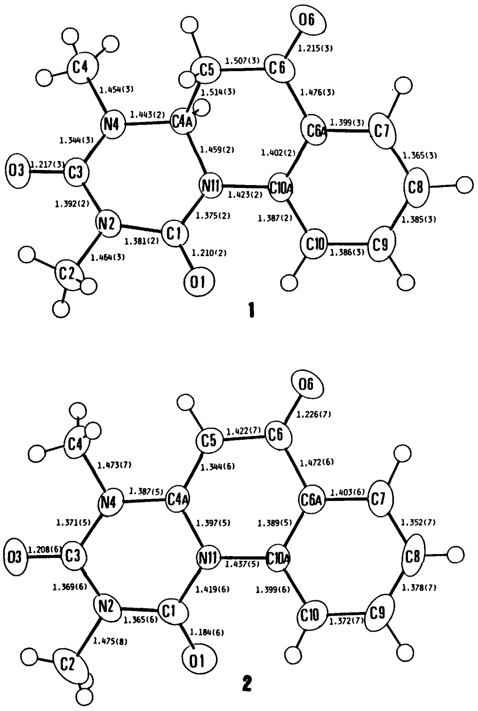


Fig. 2. Bond lengths (l/Å) of the compound **1** and **2**. Standard deviations in parentheses refer to the least significant digit.

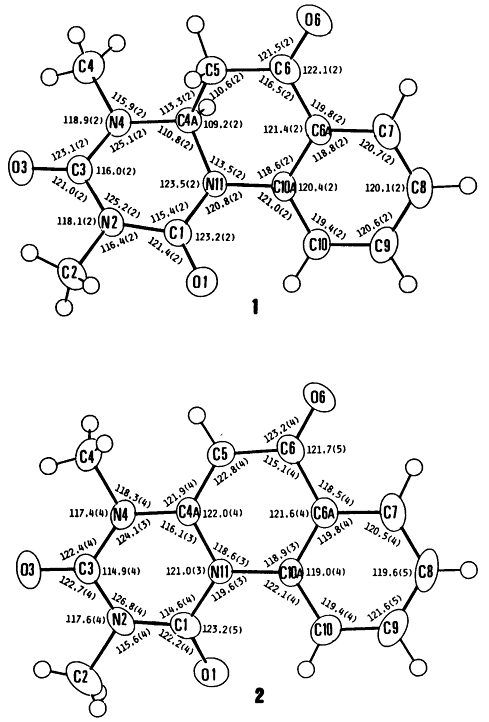


Fig. 3. Bond angles (ϕ/°) of the compound **1** and **2**. Standard deviations in parentheses refer to the least significant digit.

situation is also observed between the C(sp^2)–N bond length and the initial EI mass fragmentation in the related structure of caffein.[8,9] This feature suggests that detailed information about bond lengths in crystals is important for mechanistic studies of reactions,[10] including initial EI mass fragmentation in a gas phase.

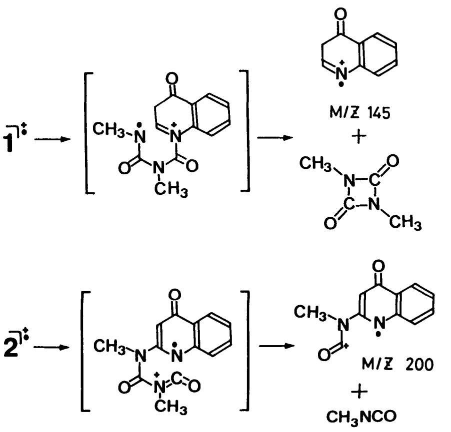


Fig. 4. Main initial EI mass fragmentations of the compound **1** and **2**.

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11) As a general expression, $B_{eq}=4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.