X-Ray Molecular Structure of 1-Cyano-7,8-benzo-11-oxatricyclo-[4.2.2.1^{2,5}]undeca-3,7,9-triene†

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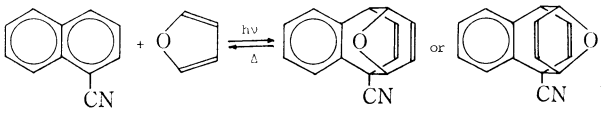
$C_{15}H_{11}ON$, *M.W.* 221.17, monoclinic, space group $P2_1/c$, $a=9.451(1)$, $b=8.267(1)$, $c=14.336(2)$ Å, $\beta=94.37(1)°$, $D_m=1.31$, $D_c=1.32$ g cm^{-3}, $Z=4$, $R=0.088$ for 1300 non-zero reflections. The molecule has an *endo*-configuration, and the furan ring has an envelope form.

Photoreaction between 1-naphthonitrile and furan gave a single cycloaddition product, although *endo*- and *exo*-isomers were expected to be formed.[1)]



exo-form *endo*-form

In order to determine the stereochemistry of the cycloadduct, an X-ray analysis of the product has been carried out.

Experimental

For the data collection, a crystal with suitable size was mounted on a G.E. single crystal orienter equipped on a Rigaku SG-2 goniometer. Stationary crystal-stationary counter method was applied. During the data collection the intensity of the standard reflections decreased; as it did so uniformly with time, a linear correction factor was applied. 1397 unique data collected up to $2\theta=110°$ were then corrected for Lp effect but not for absorption [μ(Cu $K\alpha$)$=6.70$ cm^{-1}]. The structure was solved by the symbolic addition method.[2)] Signs of 181 $|E|$'s ($|E|>1.4$) were determined, and all the non-hydrogen atoms

TABLE 1. FRACTIONAL ATOMIC COORDINATES ($\times 10^4$ for C, N, and O atoms and $\times 10^3$ for H atoms) AND THERMAL PARAMETERS WITH e.s.d.'s IN PARENTHESES

Anisotropic thermal parameters ($\times 10^4$) expressed in the form: $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$.

Atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	2756(4)	9468(4)	4979(2)	190(6)	102(6)	46(2)	−66(10)	28(6)	−25(6)
N	1952(6)	4576(6)	6412(3)	270(10)	178(10)	48(3)	−51(16)	45(9)	31(9)
C(1)	3253(6)	6508(6)	3440(3)	143(8)	113(9)	37(3)	−60(14)	13(7)	7(8)
C(2)	3225(7)	5868(7)	2544(4)	191(10)	161(10)	35(3)	−9(17)	23(8)	−5(9)
C(3)	2536(6)	4412(7)	2346(4)	181(9)	144(10)	40(3)	12(16)	−1(8)	−29(9)
C(4)	1894(7)	3606(6)	3022(4)	194(10)	101(9)	51(3)	−13(15)	−32(9)	−46(9)
C(5)	1921(6)	4210(6)	3939(3)	154(8)	104(8)	40(3)	−9(14)	6(8)	−3(8)
C(6)	2596(5)	5675(6)	4138(3)	132(7)	92(8)	30(3)	−15(13)	4(7)	−4(7)
C(11)	2764(6)	6482(6)	5104(3)	137(7)	104(8)	31(3)	−32(13)	5(7)	−4(8)
C(12)	4312(6)	6903(6)	5284(4)	154(8)	109(9)	42(3)	−28(14)	2(8)	−11(8)
C(13)	4945(6)	7701(7)	4616(4)	154(8)	118(9)	53(3)	−69(15)	8(8)	−28(9)
C(14)	4001(6)	8099(7)	3728(4)	175(9)	131(9)	40(3)	−2(15)	4(8)	−2(9)
C(21)	2894(7)	9450(6)	3973(4)	195(10)	96(9)	48(3)	−50(15)	29(9)	15(9)
C(22)	1409(6)	9044(6)	3615(4)	170(9)	102(9)	54(3)	−6(15)	11(8)	−2(9)
C(23)	750(6)	8258(6)	4268(4)	156(8)	113(9)	53(3)	22(14)	27(18)	−2(9)
C(24)	1822(6)	8137(6)	5116(3)	173(9)	104(8)	35(3)	−34(14)	12(8)	−16(8)
C(31)	2307(7)	5383(7)	5840(4)	212(10)	120(9)	36(3)	−3(16)	6(9)	−16(8)
H(2)	364(5)	635(6)	207(3)	1.6(11)					
H(3)	240(6)	393(7)	167(4)	4.0(15)					
H(4)	146(5)	269(6)	289(3)	1.6(11)					
H(5)	130(6)	370(7)	442(4)	3.6(14)					
H(12)	502(6)	642(7)	587(4)	3.5(14)					
H(13)	625(5)	792(7)	463(4)	2.7(13)					
H(14)	463(7)	865(9)	316(5)	6.1(19)					
H(21)	306(6)	66(7)	375(4)	3.5(14)					
H(22)	83(6)	926(7)	297(4)	3.9(15)					
H(23)	−38(6)	783(8)	424(4)	4.7(16)					
H(24)	141(5)	838(6)	574(3)	2.2(12)					

† Read at the 28th National Meeting of the Chemical Society of Japan, Tokyo, April 1973.

were located in the *E*-map. All the H atoms were located by difference syntheses. The refinements was carried out by block-diagonal least-squares (*HBLS V*)[3] with anisotropic temperature factors for non-hydrogen atoms. The final *R* values were 0.088 for 1300 non-zero and 0.094 for all reflections. Atomic scattering factors for C, N, and O were taken from Hanson and coworkers,[4] and H from Stewart and coworkers.[5] The final atomic parameters are listed in Table 1.††

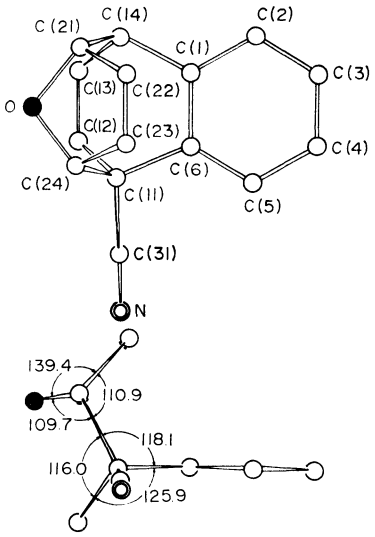


Fig. 1. Molecular structure with the numbering scheme of atoms.

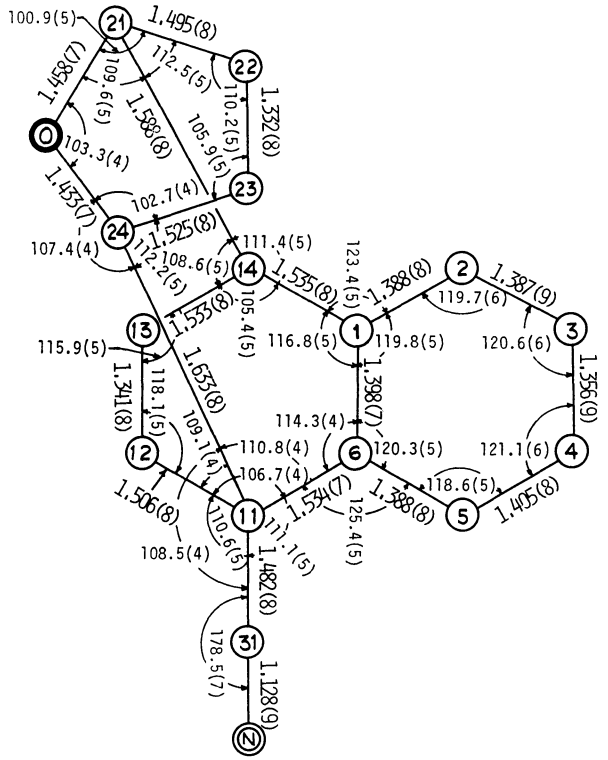


Fig. 2. Bond lengths and bond angles with e.s.d's in parentheses.

†† A Table of observed and calculated structure factors are kept as Document No. 7922 at the Chemical Society of Japan.

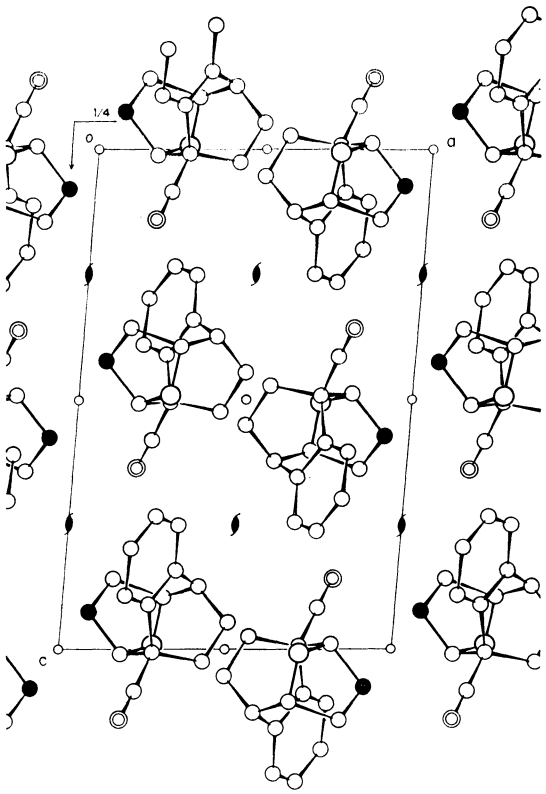


Fig. 3. Crystal structure projected along the b axis.

Results and Discussion

The molecular structure is shown in Fig. 1, which indicates that the cycloadduct has the *endo*-configuration. Bond lengths and bond angles are given in Fig. 2. The C(11)–C(24) and C(14)–C(21) bonds [1.633(8) and 1.588(8) Å, respectively] involved by the photocycloaddition are comparable with those observed in photodimers of anthracene [1.62(2) Å],[6] 2-methoxynaphthalene [1.610(5) Å][7] and 9-anthracenecarbaldehyde[1.61(1) Å],[8] which are longer than the usual $C(sp^2)$–$C(sp^3)$ bond length. The furan ring has an envelope form, the O atom is located by 0.58 Å out of the plane containing C(21) through C(24) atoms. The dihedral angle between the planes defined by O, C(21), and C(24) and C(21), C(22), C(23), and C(24) is 139.4°. The dihedral angle between C(1), C(6), C(11), and C(14) and C(11), C(12), C(13), and C(14) planes is 125.9° (Fig. 1).

The crystal structure is shown in Fig. 3. No close intermolecular atomic contact less than usual van der Waals distance can be observed.

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