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The Molecular Structure of 1-Phenoxy-1,2,2a,8b-tetrahydrocyclobuta[*a*]naphthalene-8b-carbonitrile

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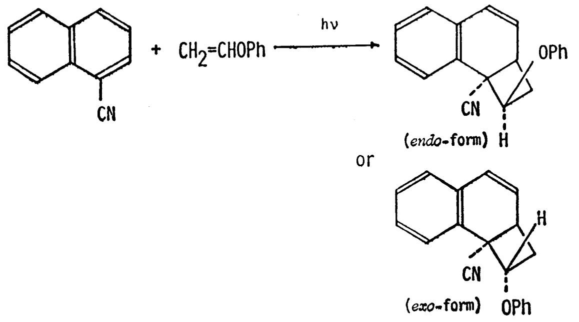
The molecular structure of the sole photocycloaddition product of α-naphthonitrile with phenyl vinyl ether, $C_{19}H_{15}ON$ was determined by means of X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$, unit-cell dimensions are $a=11.563(2)$, $b=9.826(1)$, $c=14.324(2)$ Å, $\beta=113.46(1)°$, $Z=4$. The structure was solved by the direct method, the final R value being 0.042 for 2022 non-zero reflections. The molecule has an *endo*-configuration, and the cyclobutane ring is puckered.

Recently, Pac and co-workers found that the photoreaction of α-naphthonitrile with alkyl vinyl ethers ($CH_2=CHOR$, R: Me or Et) affords both the *endo-* and *exo*-cycloadducts,[1)] whereas the (4+4) photocycloaddition of furan to α-naphthonitrile is highly stereoselective and remarkably dependent on solvent used.[2)] These facts suggested the enhanced stereoselectivity on the photocycloaddition of α-naphthonitrile with phenyl vinyl ether.



A sole cycloadduct has been obtained by the phtoreaction in question.[3)] However, spectroscopic studies failed to characterize the cycloadduct to have *endo-* or *exo*-form (Scheme), and X-ray crystal structure analysis of the cycloadduct has been carried out in order to determine the exact configuration.

Experimental

Crystal Data. $C_{19}H_{15}ON$, mp 115.5—116.5 °C, *F.W.* 273.3, $F(000)=576$, monoclinic, space group $P2_1/c$, $a=11.563(2)$, $b=9.826(1)$, $c=14.324(2)$ Å, $\beta=113.46(1)°$, $V=1493.1(3)$ Å^3, $D_m=1.22$ g cm^{-3} (25 °C, aqueous solution of potassium tartarate), $Z=4$, $D_c=1.22$ g cm^{-3}.

Unit-cell dimensions and reflection intensities were measured on a Rigaku automated, four-circle diffractometer using graphite monochromatized Cu *Kα* radiation. A parallelepiped, transparent crystal with dimensions of *ca.* 0.2×0.3×0.1 mm^3 was used.

The θ-2θ scan technique was employed for the intensity data collection at a 2θ rate of 2° min^{-1}. Backgrounds were measured for 7.5 s before and after the scan of each peak. In total 2209 independent reflections were collected up to $2\theta \leqq 120°$, of which 184 were considered unobserved. Intensity data were corrected for Lp effect but not for absorption [$\mu(\mathrm{Cu})=6.08$ cm^{-1}].

Solution and Refinement of the Structure

The structure was solved by the direct method. From the Wilson plot average temperature factor and scale factor were obtained. A set of 284 $|E|$'s($|E|\geqq 1.5$) were used with the *MULTAN* program[4)] to establish the phase relationship. From the E map (ABSFOM 1.2422) all the non-hydrogen atoms could be located. The positional and isotropic thermal parameters of these atoms were refined by the block-diagonal least-squares procedure (*HBLS* V[5)]). After eight cycles of refinement (R=0.158), anisotropic thermal parameters were introduced; five cycles of refinement reduced the R to 0.094. All the H atoms were located on a difference Fourier map. The refinement was continued including these H atoms with isotropic thermal parameters. The function minimized was $(\sum w|F_o|-k|F_c|)^2$, where k is a single scale factor and $w=\{\sigma_{cs}(F_o)+a|F_o|+b|F_o|^2\}^{-1}$ (σ_{cs}: standard deviation determined from the counting statistics). The R value converged to 0.053. However, in the range $7.0\leqq|F_o|\leqq 20.0$ the quantity minimized showed an anomaly. The $30\bar{2}$, 111, and 402 reflections which have extraordinarily large $|F|$'s were then excluded, and the weights of Hughes,[6)] $w=(F_{max}/|F_o|)^{-2}$ for $|F_o|>F_{max}$ and $w=1$ for $|F_o|\leqq F_{max}$ ($F_{max}=15.0$ in the present study), were introduced in the next stage. The refinement converged normally to $R=0.042$ ($R_w=0.052$). Atomic scattering factors for C, N, and O were taken from those of Hanson and coworkers,[7)] and that of H from Stewart and coworkers.[8)] The final atomic parameters are given in Table 1.[†††]

Results and Discussion

Figure 1 shows an *ORTEP* plot[9)] of the molecule. Bond lengths and bond angles are given in Fig. 2.

The remarkable feature of the structure is that the photocycloadduct of α-naphthonitrile with phenyl vinyl ether has the *endo*-configuration (Scheme). This result suggests an existence of the exciplex of the phenyl vinyl ether as a photoreaction intermediate.[3)]

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[†††] The Table of observed and calculated structure factors are kept as Document No. 8007 at the Chemical Society of Japan.

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:
$\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	2868(1)	1495(1)	4099(1)	74(1)	94(1)	55(1)	−11(2)	19(1)	2(2)
N	3786(2)	5716(2)	5313(1)	110(2)	141(2)	111(1)	−73(3)	100(3)	−82(3)
C(1)	2446(1)	4069(2)	3855(1)	74(1)	88(2)	57(1)	−9(3)	51(2)	3(2)
C(2)	1157(1)	3853(2)	3883(1)	70(1)	92(2)	57(1)	−5(3)	43(2)	−22(2)
C(3)	75(2)	4354(2)	3084(1)	77(2)	103(2)	80(1)	25(3)	37(2)	−21(3)
C(4)	173(2)	5058(2)	2212(2)	131(2)	142(3)	79(1)	92(4)	31(3)	59(3)
C(5)	1223(2)	5117(2)	2070(2)	159(3)	147(3)	84(2)	74(4)	90(3)	93(3)
C(6)	2379(2)	4435(2)	2771(1)	115(2)	124(2)	71(1)	6(3)	88(3)	42(3)
C(7)	2551(2)	2909(2)	2604(1)	118(2)	145(2)	56(1)	37(4)	80(3)	9(3)
C(8)	3145(1)	2737(2)	3751(1)	69(1)	102(2)	55(1)	−1(3)	46(2)	4(2)
C(9)	3190(2)	4998(2)	4674(1)	76(2)	103(2)	80(1)	−22(3)	74(2)	−19(3)
C(10)	1058(2)	3231(2)	4708(1)	84(1)	125(2)	63(1)	−26(3)	64(2)	−31(3)
C(11)	−113(2)	3081(2)	4755(2)	123(2)	155(3)	88(2)	−76(4)	130(3)	−71(3)
C(12)	−1179(2)	3572(2)	3963(2)	76(2)	165(3)	129(2)	−45(4)	102(3)	−122(4)
C(13)	−1077(2)	4196(2)	3148(2)	77(2)	154(3)	108(2)	19(4)	53(3)	−52(4)
C(14)	3624(1)	1052(2)	5066(1)	69(1)	95(2)	54(1)	25(3)	47(2)	−3(2)
C(15)	4527(2)	1840(2)	5790(1)	88(2)	111(2)	63(1)	24(3)	27(2)	−18(3)
C(16)	5238(2)	1264(2)	6734(1)	110(2)	174(3)	59(1)	82(4)	22(3)	−39(3)
C(17)	5051(2)	−51(2)	6953(2)	157(3)	178(3)	60(1)	151(5)	80(3)	41(3)
C(18)	4148(2)	−821(2)	6223(2)	162(3)	134(3)	82(1)	73(4)	122(3)	58(3)
C(19)	3433(2)	−275(2)	5283(1)	114(2)	107(2)	72(1)	7(3)	81(3)	10(3)
H(4)	−61(2)	550(3)	172(2)	8.2(6)					
H(5)	125(2)	556(3)	144(2)	7.6(6)					
H(6)	318(2)	496(2)	287(2)	5.8(5)					
H(7A)	304(2)	270(2)	221(2)	5.6(5)					
H(7B)	169(2)	242(2)	232(2)	5.0(5)					
H(8)	408(2)	293(2)	403(2)	3.5(4)					
H(10)	183(2)	289(2)	526(2)	3.9(5)					
H(11)	−14(2)	265(2)	535(2)	5.4(5)					
H(12)	−199(2)	349(3)	403(2)	7.0(5)					
H(13)	−187(2)	454(2)	257(2)	6.3(4)					
H(15)	466(2)	277(2)	565(2)	4.6(4)					
H(16)	586(2)	186(3)	724(2)	7.0(6)					
H(17)	551(2)	−44(3)	763(2)	7.7(6)					
H(18)	402(2)	−178(3)	635(2)	7.8(6)					
H(19)	279(2)	−82(2)	476(2)	5.7(5)					

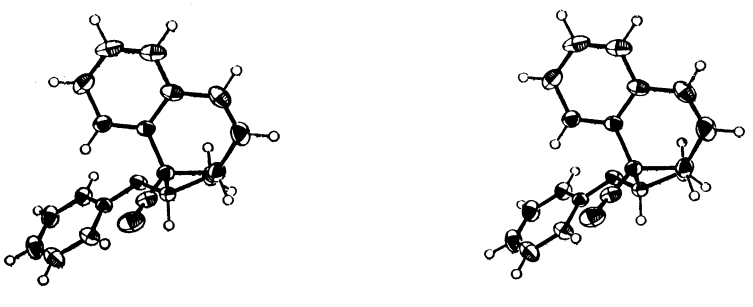

Fig. 1. A stereoscopic drawing of the molecule.
Non-hydrogen atoms are drawn as thermal ellipsoids with 30% probability and H atoms are circles with $B=1.2$ Å^2

The cyclobutane ring C is puckered, dihedral angle between the plane defined by C(6), C(1), and C(8) and the plane of C(6), C(7), and C(8) being 31.3°. A significant lengthening of C(1)–C(6) [1.565(3) Å] and C(1)–C(8) bonds [1.577(2) Å] is clearly observed. On the other hand C(7)–C(8) bond shows a shortening [1.516(3) Å]. As a result of the cyclobutane ring formation, ring B of the naphthonitrile moiety is no more planar, the C(1) and C(6) atoms are deviated by 0.10 and −0.14 Å out of the mean plane, respectively. Both rings A and D are planar within 0.002 Å and have normal structures. Concerning the ether

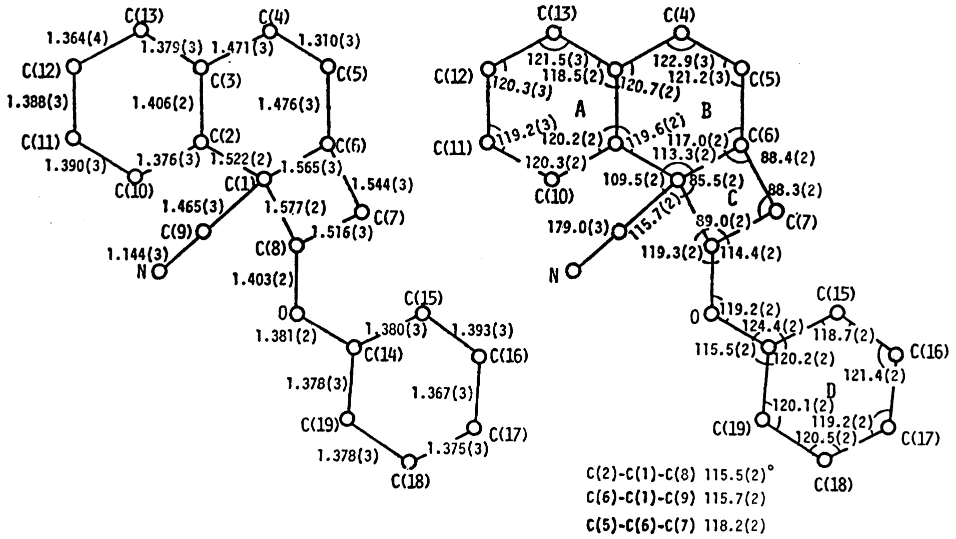

Fig. 2. Bond lengths and bond angles with e.s.d's in parentheses.

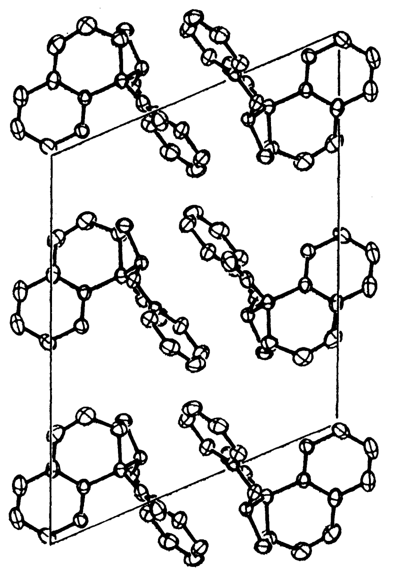

Fig. 3. Crystal structure projected along the b axis.

bond, the C(8)–O bond length [1.403(2) Å] is longer than the C(14)–O [1.381 (2) Å]. The torsion angle C(8)–O–C(14)–C(15) is −10.9°. This is considered as due to the steric interaction between H(8) and H(15) [H(8)···H(15)=2.13(3) Å].

Figure 3 shows the crystal structure projected along the b axis. No close intermolecular contact less than usual van der Waals distance is observed.

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