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The Photo-addition of Naphthalene and Acrylonitrile. An X-ray and Nuclear Magnetic Resonance Study of the Cycloadducts

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The photoaddition of naphthalene and acrylonitrile has been reinvestigated. It was found that the cyclobutane adduct described previously is *endo*-7-cyano-2,3-benzobicyclo[4.2.0]-octa-2,4-diene (7), and not the *exo*-8-cyano compound. The structure was determined from an X-ray diffraction study on the *p*-bromophenylurethane of the carbinol derived from the cyano-compound. The structural details are described. The crystallographic data are $a = 13.85(1)$, $b = 7.976(2)$, $c = 12.752(4)$ Å, $\alpha = 90.80(3)$, $\beta = 87.02(6)$, $\gamma = 90.99(5)°$ space group $P\bar{1}$, $Z = 2$ units of $C_{20}H_{18}O_2NBr$. The least-squares residual R was 0.085 for 651 X-ray reflections measured on a Syntex P1 diffractometer using graphite-monochromatized Mo radiation. The methine proton resonances in the 220 MHz n.m.r. spectrum of 7 were resolved using pyridine solvent, and the coupling constants are consistent with the structure and geometry, as derived from the X-ray work. A small fraction (7%) of 8-cyano-2,3-benzo-bicyclo[4.2.0.]octa-2,4-diene was also formed. This is tentatively assigned as the *endo* isomer, and on base treatment it isomerizes to a new compound, identified as the *exo* isomer. In contrast, the major cycloadduct 7 is recovered unchanged from base treatment. The folded geometry of the four-membered ring in these adducts apparently determines the stabilities of the epimers, and the proton–proton vicinal coupling constants.

La photoaddition du naphtalène et de l'acrylonitrile a été réétudiée. On a trouvé que l'adduit cyclo-butane précédemment décrit est l'*endo*-cyano-7 benzo-2,3 bicyclo[4.2.0] octadiène-2,4 (7) et non l'*exo*-cyano-8. La structure a été déterminée par la diffraction de rayons X sur le *p*-bromophényluréthane du carbinol dérivé du composé cyano. Des détails sur la structure sont fournis. Les données cristallo-graphiques sont: $a = 13.85(1)$ $b = 7.976(2)$, $c = 12.752(4)$ Å, $\alpha = 90.80(3)$, $\beta = 87.02(6)$, $\gamma = 90.99(5)°$, le groupe spatial est $P\bar{1}$ et $Z = 2$ unités de $C_{20}H_{18}O_2NBr$. La méthode des moindres carrés donne un R résiduel de 0.085 pour 651 réflexions de rayons X prises sur diffractomètre syntex P1, avec une radiation Mo rendue monochromatique par le graphite. Les résonances du proton méthine en r.m.n. à 220 MHz, ont été résolues avec la pyridine comme solvant; les constantes de couplage sont compatibles avec la structure et la géométrie fournies par les rayons X. Une petite fraction (7%) de cyano-8 benzo-2,3 bicyclo[4.2.0] octadiène-2,4 a été également formée. On a tenté de l'identifier à l'isomère *endo*, ce dernier s'isomérise par traitement basique en un nouveau composé identifié à l'isomère *exo*. Le cycloadduit 7 a été retrouvé inchangé après traitement basique. La géométrie plissée du cycle à quatre membres dans ces adduits détermine apparemment les stabilités des épimères et les constantes de couplage vicinal entre protons. [Traduit par le journal]

During the past few years, we have reported studies of products (1, 2) and mechanism (3, 4) of the photoaddition of naphthalene and acrylonitrile in hydroxylic solvents. The products were assigned the structures **1**, **2**, and **3**.


1, 2   3
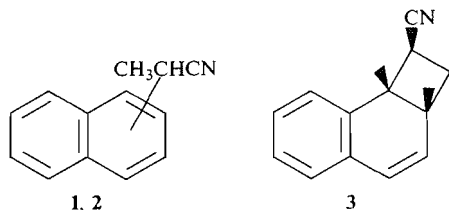
The cycloadduct was assigned the structure *exo*-8-cyano-2,3-benzobicyclo[4.2.0]-octa-2,4-diene (3) on the basis of n.m.r. evidence, equilibration behavior, and unit cell dimensions in the crystal (1, 2). However, in the course of the quantitative work on this reaction (3, 4) a second cycloadduct was found (7% yield) whose n.m.r. spectrum suggested that it was 8-cyano-2,3-benzobicyclo[4.2.0]-octa-2,4-diene. Since this minor adduct was not an epimer of the major one (see below), considerable doubt was cast on structure **3** for the latter. It was therefore decided to reinvestigate the structure of the major cyclo-adduct, and of the methods available, X-ray was chosen since this would reveal the position and stereochemistry of the cyano-group.

Results

Preparation of Derivative for X-ray Study

The major cycloadduct m.p. 98°, from photolysis of naphthalene and acrylonitrile (1, 2) was
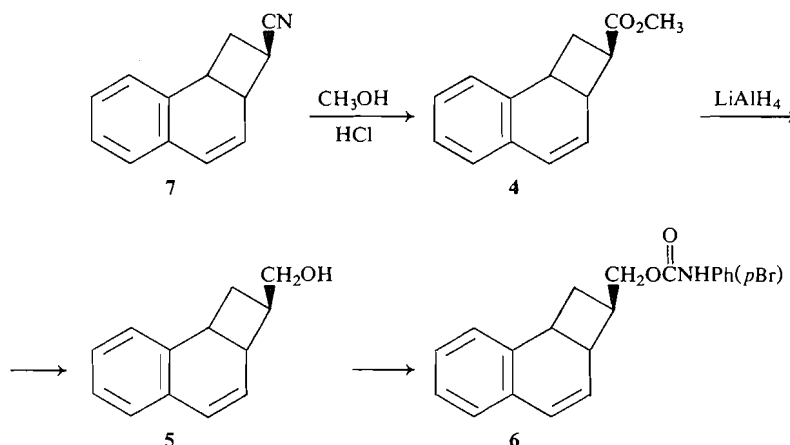
SCHEME 1

converted to the methyl ester **4** by treatment with methanol and hydrogen chloride in ether (5). Reduction of the ester with $LiAlH_4$ gave the carbinol **5** as an oil. The latter reacted with p-bromophenylisocyanate in cyclohexane at reflux to give the p-bromophenylurethane **6**, m.p. 155–157°. This derivative gave single crystals from 95% ethanol, which were used in the X-ray work. The route from the photoadduct to the derivative **6** is shown in Scheme 1.

Structure of Photoadduct

The X-ray work on the p-bromophenylurethane **6** is described in detail in the Experimental. The structure of **6** is shown in Fig. 1, and the bond distances and angles in Table 1. It can be seen that the carbinol CH_2 group in

6 is bonded at C-7, and has the *endo*-configuration. The major photoadduct must therefore be *endo*-7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene **7**, and not **3** as previously assigned.

Some interesting structural features of the benzobicyclo[4.2.0]octa-2,4-diene ring system follow from the X-ray structure. It is found, Table 2, that C-1, -2, -3, -4, -5 are coplanar, with C-6 0.16 Å out of this plane. The four-membered ring is *cis*-fused at C-1 and -6, and is non-planar, being folded about the C6–C8 diagonal by 21°. The dihedral angle in this compound is considerably smaller than in cyclobutane (33°), and somewhat smaller than in a number of substituted cyclobutanes (6, 7). The dihedral angle of 21° does allow the C-7 *endo*-substituent to adopt the more stable, equatorial conformation (7d, 8). The conformation of **7** is shown in Fig. 2.

It was reported previously (1, 2) and confirmed in more recent experiments that **7** did not epimerize on treatment with base, even though one proton was exchanged for deuterium under mild, basic conditions. We must conclude, therefore, that **7** is appreciably more stable than the (unknown) epimer. This is understandable
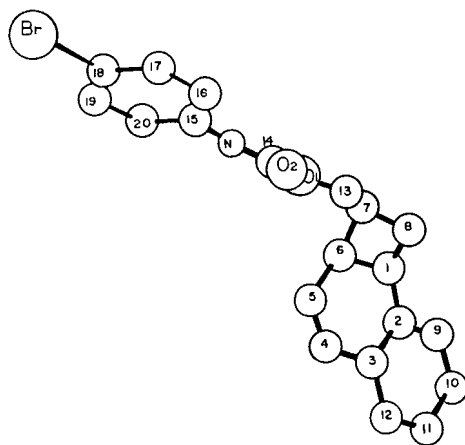

FIG. 1. Molecular structure of p-bromophenylurethane **6**; numbering agrees with that used in the Tables and in the text.
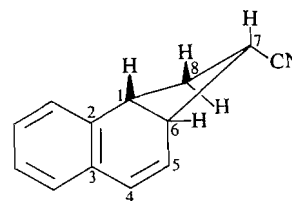

FIG. 2. Conformation of four-membered ring in photoadduct **7**.

TABLE 1. Bond distances and angles in *p*-bromophenylurethane derivative of *endo*-2,3-benzobicyclo[4.2.0]octa-2,4-diene-8-carbinol

Atoms	Bond lengths (Å)	Bond angle	(Degrees)
C1—C2	1.51(3)	C2—C1—C6	118(2)
		C2—C1—C8	115(2)
		C6—C1—C8	89(2)
C2—C3	1.47(3)	C1—C2—C3	120(2)
		C1—C2—C9	120(2)
		C3—C2—C9	120(2)
C3—C4	1.46(3)	C2—C3—C4	117(2)
		C2—C3—C12	118(2)
C1—C6	1.58(3)	C4—C3—C12	125(2)
C4—C5	1.34(3)	C3—C4—C5	127(2)
C5—C6	1.55(3)	C4—C5—C6	121(2)
C6—C7	1.60(3)	C1—C6—C5	114(2)
		C1—C6—C7	89(2)
		C5—C6—C7	113(2)
C7—C8	1.56(3)	C6—C7—C8	89(2)
		C6—C7—C13	122(2)
C8—C1	1.58(3)	C1—C8—C7	90(2)
C9—C2	1.36(3)	C2—C9—C10	120(2)
C9—C10	1.47(3)		
C10—C11	1.39(3)	C9—C10—C11	118(2)
C11—C12	1.37(3)	C10—C11—C12	122(2)
C12—C3	1.43(3)	C3—C12—C11	121(2)
C13—O1	1.45(2)	O1—C13—C7	106(2)
C13—C7	1.50(3)		
C14—O1	1.30(3)	O1—C14—O2	122(2)
C14—O2	1.25(3)	O1—C14—N	115(2)
C14—N	1.36(3)	O2—C14—N	123(2)
C15—N	1.37(3)	N—C15—C16	123(2)
C15—C16	1.44(3)	N—C15—C20	119(2)
		C16—C15—C20	118(2)
C16—C17	1.39(3)	C15—C16—C17	118(2)
C17—C18	1.40(3)	C16—C17—C18	123(2)
C18—C19	1.41(3)	C17—C18—C19	119(2)
C18—Br	1.86(2)		
C19—C20	1.38(3)	C18—C19—C20	119(2)
C20—C15	1.43(3)	C15—C20—C19	123(2)
		C12—O1—C14	119(2)
		C14—N—C15	128(2)

in terms of the geometry of **7**, since the epimer would have the cyano-group axial, if the cyclobutane ring is folded as shown.

Structure of the Minor Cycloadduct

The minor cycloadduct was present in about 7% of the total photoadduct yield, as estimated by v.p.c. analysis, and was isolated by column chromatography. The adduct **8** had m.p. 56–58° and isomerized on treatment with base to a compound **9**, m.p. 47–48°. Both **8** and **9** (and **7**) had mass spectra typical of cyclobutanes (9), in that the parent ion peaks at *m/e* 181 (3) were weak, and the base peaks at *m/e* 128 (100) corresponded to naphthalene cation. It is obvious that **8** and **9** must be the epimeric

8-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-dienes, but the question of which is which cannot be answered with certainty. However, if it is assumed that the four-membered ring is folded in the same way as in **7**, the structures of **8** and **9** can be assigned, as shown in Scheme 2.

The equilibrium composition is 88% of **9** and 12% of **8**. The cyano-group will be equatorial in the *exo*-compound, which should therefore correspond to the more stable isomer, **9**. The *endo*-isomer should therefore be the photo-adduct, **8**.

This tentative assignment is supported by the n.m.r. spectra, which are described in Table 2. In the spectrum of **9**, H-8 (α to cyano-group) appears as a quartet, *J* = 10.0 Hz. That is, all
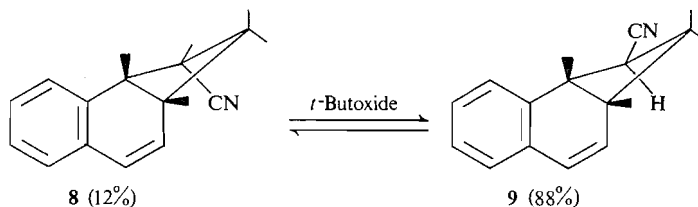
SCHEME 2

TABLE 2. Least-squares planes and out-of-plane
distances*

Atom	Out-of-plane deviations (Å)
(a) Plane defined by C-1, -2, -3, -4, -5, -9, -10, -11, -12 is $9.18X - 3.65Y + 3.08Z = 11.04$ with a standard of 0.05 Å	
C-6	0.16
C-7	−1.18
C-8	−1.58
C-13	−2.20
(b) Plane defined by C-6, -7, and -8 is $-8.6X + 4.04Y + 7.31Z = 5.64$	
C-1	−0.41
C-13	1.12
(c) Plane defined by C-1, -6, and -8 is $4.58X + 4.14Y + 5.62Z = 8.83$	
C-2	1.17
C-3	2.44
C-4	2.43
C-5	1.39
C-7	−0.41
C-9	1.10
C-10	2.28
C-11	3.46
C-12	3.56
C-13	0.27

*The acute angle between planes (a) and (c) is 21.33° and that
between (b) and (c) is 72.59°. The out-of-plane (a) distance of C-7 and
-8 support the stereochemistry proposed as does the fact C-1 and -13
are on opposite sides of plane (b). Further support is provided by the
fact that C-7 is on the opposite side of all the remaining atoms reported
out-of-plane (c) and in particular C-13.

the vicinal coupling constants for H-8 are large.
In **8** however, the H-8 resonance appears as a
doublet of triplets, $J = 6.0$ and 8.5 Hz (a
further splitting of $J = 2.0$ Hz is present, due
to coupling with H-8). The coupling constant of
6.0 Hz may be due to a vicinal equatorial–
equatorial coupling, since this is variable in
magnitude (10). All the couplings in **9** however,
should be axial–axial or axial–equatorial, and
should therefore be large (10).

To check the above assignments, a spin de-
coupling experiment was performed on **8**. The
multiplet at 3.20 δ (assigned to H-6) was irradi-
ated, and the following changes were noted. The

H-5 doublet of doublets became a doublet; the
triplet at 3.92 δ (H-1) collapsed to a broad peak,
and a small change was observed in the multiplet
at 3.45 δ (H-8).

*Interpretation of the Nuclear Magnetic
Resonance Spectrum of the Major
Cycloadduct*

The n.m.r. spectrum of **7** (CDCl$_3$) at 100 MHz
was described previously (1, 2). It was reported
that the three methine protons gave rise to a
complex multiplet at 3.54 δ, and the protons of
the methylene group gave a multiplet at 2.65 δ,
and this can be seen in Fig. 3A. No coupling
constants could be measured from these multi-
plets. Since the geometry of the four-membered
ring is known from our X-ray study, it seemed
worthwhile to obtain values for the vicinal
proton–proton coupling constants in this ring.
Interpretation of cyclobutane p.m.r. spectra is
difficult, in spite of the considerable amount of
data which is available (11), and it was of
interest to see if the spectrum of **7** could be
interpreted by taking the shape of the cyclo-
butane ring into account (10).

During deuterium exchange experiments on
7, using pyridine as solvent, it was noted that
the methine multiplet was partially resolved at
100 MHz. By utilizing this solvent, which is
known to shift protons near a polar functional
group (12), and by use of a 220 MHz instrument,
the three resonances in the methine multiplet
were resolved. The coupling constants and
chemical shifts are given in Table 3, and the
spectra in pyridine (220 MHz) and in CDCl$_3$
(100 MHz) are shown in Fig. 3.

The vicinal coupling constants for H-1 and -7
(the latter assigned by deuterium exchange) are
large (8.5–10.0 Hz), which is reasonable for
structure **7**. There is no equatorial–equatorial
splitting to these protons, and this apparently is
the only vicinal coupling in cyclobutanes which
can be small (10).
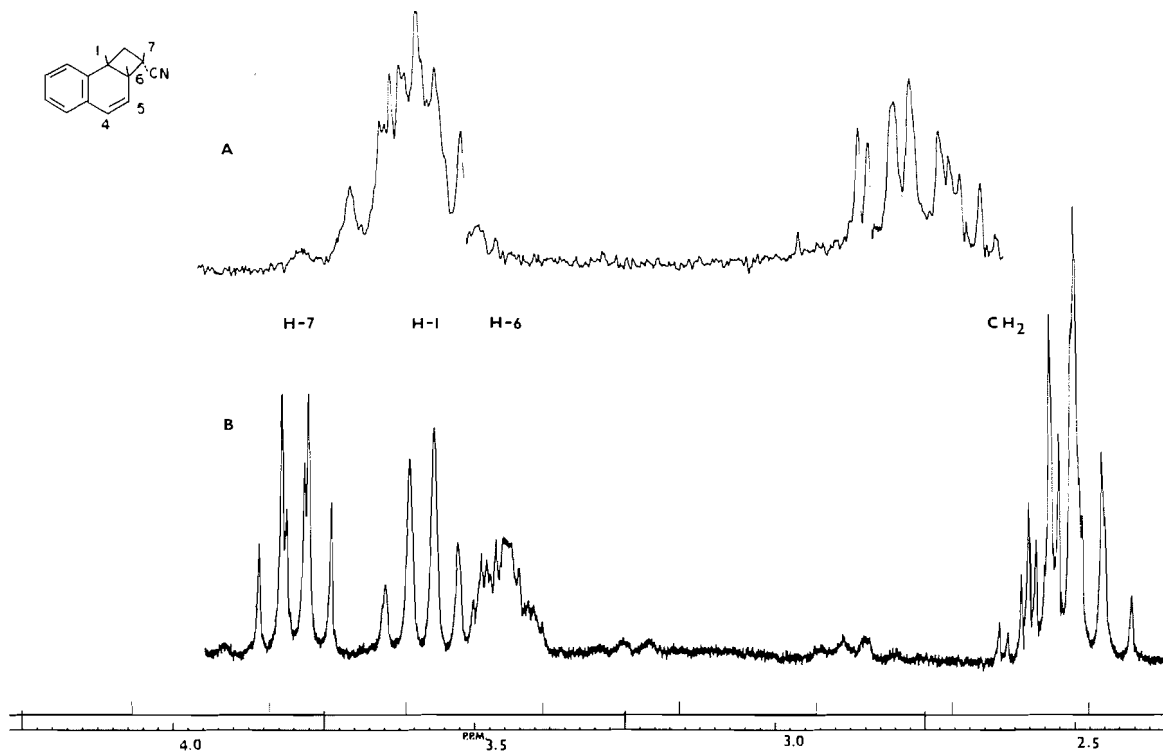
A repeat of the spin decoupling experiment

FIG. 3.   N.m.r. spectra of cycloadduct 7. (A) Spectrum at 100 MHz, $CDCl_3$ solvent; (B) spectrum at 220 MHz, pyridine solvent. The chemical shift scales for A and B are in approximate agreement, and chemical shifts should be taken from Table 2.

reported previously (2) revealed that the vinylic proton H-5 is coupled to the methine proton H-6, and not to the protons of the methylene group.

A discussion of the orientation in this photo-addition is included in the paper on substituent effects on the reaction (13).

Experimental

Materials

Reagents and solvents not listed here were obtained and purified as described previously (2). Acrylonitrile was Eastman Practical Grade, purified by the method of Bevington and Eaves (14).
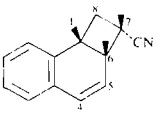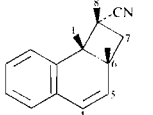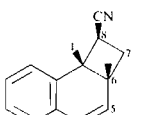
Instrumentation

N.m.r. spectra were obtained with a Varian HA-100 instrument and chemical shifts are given in p.p.m. (δ) downfield from tetramethylsilane. I.r. spectra were run on a Beckman IR-5 or on a Perkin–Elmer 337 instrument. Mass spectra were normally measured on a Hitachi-Perkin–Elmer MRU 6 instrument. V.p.c. was carried out on a Varian 204B dual column instrument, using helium at 35 ml/min. Melting points were taken on a Kofler hot stage and are reported corrected. Microanalyses were by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Photolysis of Naphthalene and Acrylonitrile

Naphthalene (1.025 g; 0.008 mol) and acrylonitrile (21.2 g, 0.4 mol) in 400 ml of 1:1 tert-butyl alcohol – iso-propyl alcohol were irradiated under argon, using the Hanovia 450 W lamp and a Pyrex filter, for 4 h. The solution was evaporated under vacuum, and the mixtures from seven identical runs were combined. The total crude yield was extracted with 250 ml of 5:1 hexane–ether mixture and filtered, and the filtrate was evaporated. The polymer-free mixture thus obtained was chromato-graphed on a 70 × 4.0 cm column of silica gel, slurry-packed in benzene, and eluted with this solvent. 200 ml fractions were collected. Fractions 1 and 2 contained naphthalene (2.15 g) and fractions 12–15 contained the substituted naphthalenes 1 and 2 (160 mg). The major cyclobutane 7 was found in fractions 16–29 (4.13 g, m.p. 97–98° from light petroleum). Fractions 30–40 contained the new cyclobutane, 8 mixed with 7 (total weight 750 mg). The latter fractions were combined and chromatographed on a 55 × 2.0 cm column of silica gel, again elution was with benzene, and 200 ml fractions were collected. Fractions 8–17 contained 500 mg of 8, m.p. 55–60°, from light petroleum. The material was homo-geneous by v.p.c. and t.l.c. Sublimation at 55–60°/0.1 mm, and further crystallization from light petroleum afforded endo-8-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (8), m.p. 56–58°.

Anal. Calcd. for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.20; H, 6.12; N, 7.69.

TABLE 3. N.m.r. spectral data for cyclobutane adducts of naphthalene and acrylonitrile

Cyclobutane isomer	Chemical shifts,* multiplet structure,† coupling constant (J)‡						
	H-1	H-4	H-5	H-6	H-7(7')	H-8(8')	Other
(structure 7)	3.61,q* $J=9.0$	6.63,d $J=10.0$	5.93,dd $J=10.0,3.0$	3.47,m*	3.82,dt* $J=8.5,10.0$	2.55,m	7.0,m
(structure 8)	4.02,t $J=9.0$	6.37,dd $J=10.0,\sim1.0$	5.75,dd $J=10.0,4.0$	3.25 sym. m	2.25,2.75 both m	3.55,ddt $J=8.5,6.0,2.0$	7.05,7.20 both m
(structure 9)	3.91,t $J=9.0$	6.40,dd $J=10.0,1.5$	5.75,dd $J=10.0,3.5$	3.25,m	2.25,2.75 both m	3.35,dq $J=9.0,1.0$	7.0-7.2 m

*Measured at 100 MHz using $CDCl_3$ as solvent, except for 7 where H-1, -6, and -7 resonances were resolved at 220 MHz in pyridine solution; shifts given in p.p.m. downfield from tetramethylsilane.
†m = multiplet; d = doublet; dd = doublet of doublets; dt = doublet of triplets; ddt = doublet of doublets of triplets; q = quartet.
‡Coupling constants (J) given in Hz.

In the i.r. the CN stretch showed at 2265 cm^{-1} (CCl_4). The n.m.r. spectrum is described in Table 2 and in the text. Analysis of the photolysis mixture by v.p.c. (5 ft × 1/8 in. of 5% QF-1 on Chromosorb W, at 170°) showed the following ratios and retention times: 7, 89%, 3.4 min; 8, 7.0% 3.9 min; 1 and 2, 4.0%, 2.6 min. The peaks of 7 and 8 overlapped and the ratio was measured using a Dupont Analog Curve Resolver.

Epimerization of endo-8-Cyano-2,3-benzobicyclo[4.2.0-]octa-2,4-diene (8)

Compound 8 (130 mg, 0.717 mmol) was dissolved in 15 ml of 0.1 M potassium *tert*-butoxide in *tert*-butyl alcohol. The mixture was stirred at ambient temperature in a nitrogen atmosphere, and the aliquots were withdrawn periodically and analyzed by v.p.c. on the above QF-1 column. A new peak of retention time 2.9 min appeared, and after 4 h of reaction, the area of this peak showed no further increase with time. This peak is identified as 9, and the equilibrium mixture of 8 and 9 contained 88% of the latter. After 6 h, the mixture was poured into ether, and the solution was washed with 0.5 N HCl, then with saturated NaCl solution, and dried ($MgSO_4$). The oil obtained on evaporation of the solvent was chromatographed on a 2 × 65 cm column of silica gel. Elution was with benzene and 200 ml fractions were collected. Fractions 5–8 contained 9 (101 mg, m.p. 46–48°) and 8 (15 mg) was recovered in fractions 10–16. *exo*-8-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene had the CN band at 2265 cm^{-1}, and the n.m.r. spectrum is described above. Sublimation at 60°/0.1 mm, and crystallization from light petroleum gave colorless prisms, m.p. 47–48°.

Anal. Calcd. for $C_{13}H_{11}N$: C, 86.15; H, 6.12; N, 7.73 Found: C, 86.26; H, 6.13; N, 7.67.

Since the retention times of 1, 2 and 9 are very similar, it is difficult to know if 9 is formed in the photolysis. Since its presence was not noted during chromatography

of the photolysis mixture, it can only be present in very minor amount.

Deuterium Exchange of endo-7-Cyano-2,3-benzobicyclo-[4.2.0]octa-2,4-diene (7)

To the cyano-compound 7 (20 mg) in dry pyridine (0.3 ml) was added 0.05 ml of 0.05 M NaOD, and the mixture was heated at 50° for 12 h. in an n.m.r. tube. Integration of the methine and methylene proton multiplets showed that one methine proton had been exchanged for deuterium. In this solution at 100 MHz the three methine proton resonances were partially resolved, and it was possible to identify the lowest field doublet of triplets with the proton removed by exchange.

Conversion of endo-7-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (7) to endo-7-Carbomethoxy-2,3-benzobicyclo[4.2.0]octa-2,4-diene (4)

A mixture of methyl alcohol and anhydrous ether (7:20) (54 ml) at 0° was saturated with HCl from a tank by bubbling the gas through for 1 h. The cyano-compound 7 (1.0298 g, 0.00568 mol) was then added, and the solution was stirred (magnetic stirrer) for 8 h. Water (20 ml) was added dropwise at 0°, the mixture was warmed at 25°, and stirred 3 h. On pouring into water (500 ml) and extracting with ether, 144 mg of ester 4 was obtained. On allowing the aqueous layer from the extraction to stand 12 h, crystals of 4 (891 mg) m.p. 84–89° were deposited. The combined products were crystallized from ethanol–water to afford *endo*-7-carbomethoxy-2,3-benzobicyclo[4.2.0]octa-2,4-diene, 1.0200 g, 84%, m.p. 91–93°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.44; H, 6.63.

LiAlH₄ Reduction of endo-7-Carbomethoxy-2,3-benzobicyclo[4.2.0]octa-2,4-diene

The ester 4 (700 mg, 3.267 mmol) in ether (20 ml) was added dropwise to a stirred slurry of lithium aluminum

TABLE 4. Atomic parameters of the p-bromophenylurethane derivative

Atom	x	y	z	$B(\text{Å}^2)$
Br	0.3752(2)	0.0754(7)	1.4106(3)	*
O-1	0.7541(10)	0.047(3)	0.891(1)	4.7(3)
O-2	0.674(1)	0.382(3)	0.973(1)	6.1(4)
N	0.661(1)	−0.047(3)	1.036(1)	3.8(4)
C-1	1.011(1)	0.101(4)	0.672(2)	4.4(5)
C-2	1.099(1)	0.287(4)	0.673(2)	4.2(6)
C-3	1.122(2)	0.436(4)	0.769(2)	4.2(5)
C-4	1.064(2)	0.369(5)	0.865(2)	5.2(6)
C-5	0.994(2)	0.181(4)	0.876(2)	4.9(6)
C-6	0.965(2)	0.004(4)	0.781(2)	4.8(5)
C-7	0.861(1)	0.075(4)	0.741(2)	4.8(5)
C-8	0.913(1)	0.240(4)	0.650(2)	4.8(5)
C-9	1.152(2)	0.334(5)	0.581(2)	5.9(6)
C-10	1.231(2)	0.536(5)	0.578(2)	6.6(6)
C-11	1.249(2)	0.677(5)	0.670(2)	5.7(6)
C-12	1.198(2)	0.630(5)	0.763(2)	5.4(6)
C-13	0.788(1)	0.229(4)	0.808(2)	4.1(5)
C-14	0.696(2)	0.139(5)	0.966(2)	4.5(5)
C-15	0.594(1)	−0.010(4)	1.118(2)	3.9(5)
C-16	0.521(1)	0.192(4)	1.120(2)	4.5(5)
C-17	0.457(1)	0.210(4)	1.208(2)	4.6(5)
C-18	0.460(2)	0.035(5)	1.293(2)	5.5(6)
C-19	0.533(2)	−0.159(5)	1.293(2)	6.1(6)
C-20	0.597(2)	−0.183(5)	1.206(2)	5.3(6)

*Anisotropic thermal components (Å²) for Br are:

B_{11}†	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
7.06	10.03	8.18	−0.64	0.94	−1.28

†The expression for the thermal ellipsoid used in the structure amplitude calculations includes the terms

$$\exp\left[-\tfrac{1}{4}(h^2 a^{*2} B_{11} + 2hka^* b^* B_{12} + \ldots)\right].$$

hydride (2.0 g) in ether (100 ml). The mixture was stirred and heated under reflux for 12 h. Excess hydride was decomposed by the dropwise addition of water, and the ether was filtered and dried (MgSO₄). Evaporation gave an oil (524 mg, 85%) which declined to crystallize, but showed a broad i.r. absorption in the 3000–3500 cm⁻¹ region (OH). This was assumed to be 2,3-benzobicyclo-[4.2.0]octa-2,4-dienyl-endo-7-carbinol (5) and was converted to the required derivative without further purification.

Preparation of the p-Bromophenylurethane of Carbinol (7)

The carbinol 5 (245 mg, 1.287 mmol) dried by azeotropic distillation of benzene, and p-bromophenylisocyanate (274 mg, 1.383 mmol) in cyclohexane (20 ml) were heated under reflux for 1 h. Crystals were deposited while the solution was still hot. The mixture was cooled and filtered to afford 272 mg (55%) of the p-bromophenylurethane of 5, which gave needles, m.p. 155–157°, from 95% ethanol.

Anal. Calcd. for C₂₀H₁₈O₂NBr: C, 62.50; H, 4.72; N, 3.65; Br, 20.80. Found: C, 62.43; H, 4.64; N, 3.54; Br, 20.92.

These crystals were used in the X-ray study described below.

Description of X-ray Work on p-Bromophenylurethane (6)

Crystal Data

C₂₀H₁₈O₂NBr   f.w. = 384.26

Triclinic, space group $P\bar{1}$ with a = 13.85(1), b = 4.976(2), c = 12.752(4) Å, α = 90.80(3), β = 87.02(6), γ = 90.99(5)°, V = 877.44 Å³ D_o = 1.39 ± 0.08 g/cm³, Z = 2, D_c = 1.45 g/cm³ (20 °C, λ(MoKα) = 0.71069 Å).

The derivative was crystallized from methanol–chloroform to obtain suitable plate-shaped crystals. The dimensions of the unit cell were obtained from a least-squares refinement of 15 values of 2θ measured with MoKα radiation using a Syntex automatic diffractometer. The calculated density assuming two molecules per unit cell agrees with the density measured using a solution of potassium iodide in water, and this leads to the space group $P\bar{1}$.

A crystal with dimensions 0.02 × 0.03 × 0.08 mm was used to collect data on the Syntex diffractometer. The MoKα used for intensity data collection was monochromatized using graphite. All the data are a hemisphere with a maximum radius defined by 2θ ≤ 35° were recorded using a θ–2θ scan with a scan rate determined by the intensity at the peak and scan range dependent upon the value of θ. Backgrounds were recorded on either side of the peak and used to determine the integrated

intensity together with an estimated standard deviation based upon counting statistics. The final reflections whose intensity were less than 36 were regarded as unobserved. Of the total 1113 reflections, 651 had observable intensities. The data were corrected for Lorentz and polarization but not absorption.

The bromine atom position was determined from the Patterson function. The signs determined from the subsequent structure factor calculation were used to calculate an electron density map from which the remaining atoms were found. The structure was further refined utilizing full matrix least squares programs. This and other calculations were done using 'X-ray 67' program system for X-ray crystallography published by the University of Maryland and adopted for use with the CDC 6400 by H. D. Grundy. The atomic scattering curves were taken from the International Tables for X-ray Crystallography (15). Weights, ω, were chosen so that $\omega|F_o - F_c|^2$ would locally be independent of the, F_o, observed structure factor and the function obtained was $\omega = [15 - 0.05|F_o|]^{-1/2}$. The unobserved reflections were weighted as the observed were and also included in the refinement. The final R value is 0.105 while the least-squares residual is 0.115.[1] The refinement was terminated when the calculated shifts were less than 1/3 of the estimated standard deviations. A final difference synthesis showed no missing structural features although peaks as 1/5 of a carbon atom were noted.

The final atomic parameters are recorded in Table 4, and the observed and calculated structure factors are compared in Table 5.[2] Table 1 contains a list of the pertinent bond lengths and angles with standard deviations calculated from the standard errors derived from the least-squares matrix. The structure is shown in Fig. 1.

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[1]The weighted $R = \left\{ \dfrac{\Sigma\omega|F_o - F_c|^2}{\Sigma\omega|F_o^2|} \right\}^{1/2}$

[2]These tabular data (Table 5) are available from the Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Canada K1A 0S2.

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