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Synthesis and Molecular Structure of the 2:1-Cycloadduct of 1-Methoxy-2-benzopyrylium-4-olate with Acenaphthylene

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The Cu(acac)$_2$-catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone in the presence of acenaphthylene gave a 2:1-cycloadduct of the corresponding carbonyl ylide, 1-methoxy-2-benzopyrylium-4-olate, with acenaphthylene along with *exo*- and *endo*-1:1-adducts. The molecular structure of the 2:1-adduct was determined by means of X-ray analysis. The colorless crystals of the adduct are triclinic with the space group $P\bar{1}$,and with the unit-cell dimensions of a=12.104(2), b=12.477(3), c=9.112(2) Å, α=102.98(3), β=110.16(2), γ=70.65(1)°, and Z=2. The structure was determined by direct methods and refined by block-diagonal least-squares methods. All hydrogen atoms were revealed by a difference-Fourier synthesis, and further least-squares refinement gave the final R value of 0.057 for 3681 observed reflections. The configurations of methine protons obtained by X-ray methods are compatible with the NMR coupling pattern of the adduct.

1,3-Dipolar cycloadditions of carbonyl ylide with acetylenic, ethylenic, and carbonyl compounds have been studied extensively from the theoretical and synthetic interests.[1] The authors have reported that 1-methoxy-2-benzopyrylium-4-olate (**3**) gave 1,3-dipolar cycloadducts with carbonyl compounds in the Cu(acac)$_2$-catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone (**1**).[2] In the previous study of this series, the yields of *exo*- and *endo*-1:1-adducts (**4a** and **4b**) of (**3**) with acenaphthylene were reported to be not so high.[3] This may be attributed to the competitive reactions of the 1:1-adducts (**4**) and acenaphthylene toward the carbonyl ylide intermediate (**3**). In order to investigate the possibility of the reaction of the 1:1-adducts with (**3**), the decomposition of *o*-methoxycarbonyl-α-diazoacetophenone (**1**) was reexamined in the presence of acenaphthylene giving the expected 2:1-adduct (**5**), of which the structure was determined by X-ray analysis.

Table 1. Crystal data of the 2:1-adduct

Crystal system	Triclinic
Space group	$P\bar{1}$
a	12.104(2) Å
b	12.477(3)
c	9.112(2)
α	102.98(3)°
β	110.16(2)
γ	70.65(1)
V	1209.3(2) Å^3
Z	2
Dm	1.386 Mg m^{-3}
Dx	1.377 Mg m^{-3}
μ(Cu $K\alpha$)	0.79 mm^{-1}
Scan method	θ—2θ
Scan speed in ω	4° min^{-1}
Scan width	1.4°+0.15° tan θ
Background	2×4 s
2θmax(Cu $K\alpha$)	125°
No. of Reflections	3863 3681(except $\lvert F_o \rvert$=0)
Crystal size	0.3×0.3×0.2 mm^3

Experimental

The ^{1}H NMR and ^{13}C NMR spectra of the 2:1-adduct were measured on a Brucker NMR spectrometer, model MA 360 in CDCl$_3$, using TMS as an internal standard.

The Cu(acac)$_2$-catalyzed Decomposition of (1) in the Presence of Acenaphthylene. A benzene solution of **1** (6 mmol) was added drop by drop into a benzene solution of acenaphthylene (6 mmol) and Cu(acac)$_2$ (0.6 mmol) at 80 °C under stirring in N$_2$ atmosphere. The reaction products were isolated by column chromatography on silica gel using benzene as an eluent. Colorless crystals (**5b**; 1.56 mol, 26%) were obtained besides the *exo*- (**4a**; 16%) and *endo*-1:1-adducts (**4b**; 25%): (**5b**); colorless crystals; mp 165—166 °C; IR (KBr) 1709 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=3.50 (s, 3H, OCH$_3$), 4.04 (dd, 1H, Ha, $J_{a,b}$=6.7, $J_{a,4}$=1.3 Hz), 4.05 (s, 3H, OCH$_3$), 4.39 (dd, 1H, Hb, $J_{a,b}$=6.7, $J_{b,c}$=1.3 Hz), 4.67 (d, 1H, Hc, $J_{b,c}$=1.3 Hz), 5.19 (s, 1H, Hd), 6.28 (d, 1H, H$_{17}$, $J_{17,18}$=7.8 Hz), 6.95 (t, 1H, H$_{18}$, $J_{17,18}$=$J_{18,19}$=7.8 Hz), and 7.1—8.0 (m, 11H, Ar); ^{13}C NMR (CDCl$_3$) 48.56 (d, C$_2$), 50.27 (q, C$_{22}$), 53.65 (q, C$_{32}$), 61.52 (d, C$_{13}$), 80.83 (s, C$_{15}$), 86.90 (d, C$_{14}$), 88.20 (d, C$_{23}$), 107.63 (s, C$_1$), 119.82 (s, C$_{31}$), 191.44 (s, C$_{24}$), and 21 signals in the region of δ=118.69—145.68. Found: C, 76.21; H, 4.87%. Calcd for C$_{32}$H$_{24}$O$_6$: C, 76.18; H, 4.80%.

X-Ray Crystal Analysis of 5. The crystal data of **5** are listed in Table 1 along with the experimental details. The X-ray intensity data were measured on a Rigaku four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation. The number of nonzero reflections used in the structural determination were 3681.

The space group $P\bar{1}$ was confirmed by a statistical distribution of E values and a successful refinement of the structure.

Using 300 reflections with $\lvert E \rvert \geq 1.78$, the crystal structure was determined by direct methods with the MULTAN 78 program.[6] The E-map computed with the phase set of the highest combined figure of merit (2.708) revealed the positions of all the non-hydrogen atoms. The isotropic refinement, followed by anisotropic refinement reduced R to 0.094. The hydrogen atoms were located on a difference map and their positional parameters were refined together with isotropic thermal parameters, while the other atoms were refined anisotropically by block-diagonal least-squares. The final R value was 0.057. The function minimized was

Table 2-A. Atomic positional ($\times 10^4$) and thermal parameters for the non-hydrogen atoms of the 2:1-adduct

Atom	x	y	z	$B_{eq}/\text{Å}^2$
O(1)	2670(1)	8299(1)	2403(2)	4.4
O(2)	2269(1)	7013(1)	3473(2)	3.6
O(3)	1454(1)	4343(1)	1636(2)	3.5
O(4)	2434(1)	4038(1)	4174(2)	3.8
O(5)	852(1)	3225(1)	2746(2)	4.2
O(6)	5202(1)	3755(1)	3527(2)	4.9
C(1)	2137(2)	7401(2)	2030(3)	3.6
C(2)	738(2)	7809(2)	1292(3)	3.5
C(3)	93(2)	8967(2)	2002(3)	3.7
C(4)	146(2)	10052(2)	2031(3)	4.7
C(5)	−613(3)	10983(2)	2782(4)	5.6
C(6)	−1397(2)	10841(2)	3456(3)	5.0
C(7)	−1476(2)	9730(2)	3429(3)	4.3
C(8)	−2215(2)	9419(2)	4083(3)	4.7
C(9)	−2177(2)	8300(2)	3970(4)	4.8
C(10)	−1399(2)	7395(2)	3211(3)	4.4
C(11)	−663(2)	7666(2)	2577(3)	3.5
C(12)	−712(2)	8822(2)	2692(3)	3.6
C(13)	298(2)	6926(2)	1779(3)	3.4
C(14)	1469(2)	6287(2)	2972(3)	3.4
C(15)	2199(2)	5128(2)	2303(3)	3.3
C(16)	2674(2)	5294(2)	1052(3)	3.5
C(17)	3043(2)	4392(2)	−50(3)	4.0
C(18)	3435(2)	4580(2)	−1203(3)	4.7
C(19)	3447(2)	5671(3)	−1285(3)	5.0
C(20)	3056(2)	6582(2)	−219(3)	4.5
C(21)	2686(2)	6403(2)	966(3)	3.7
C(22)	3949(2)	8003(2)	3235(4)	5.7
C(23)	3167(2)	4540(2)	3732(3)	3.6
C(24)	4223(2)	3597(2)	3317(3)	3.8
C(25)	3951(2)	2480(2)	2609(3)	3.8
C(26)	4863(2)	1507(2)	2307(3)	4.7
C(27)	4561(3)	492(2)	1633(4)	5.4
C(28)	3366(3)	456(2)	1216(4)	5.7
C(29)	2449(2)	1420(2)	1497(3)	4.9
C(30)	2751(2)	2432(2)	2237(3)	3.8
C(31)	1834(2)	3505(2)	2693(3)	3.5
C(32)	−162(2)	4152(2)	2999(3)	5.0

Table 2-B. Atomic potential ($\times 10^3$) and thermal parameters for the hydrogen atoms of the 2:1-adduct

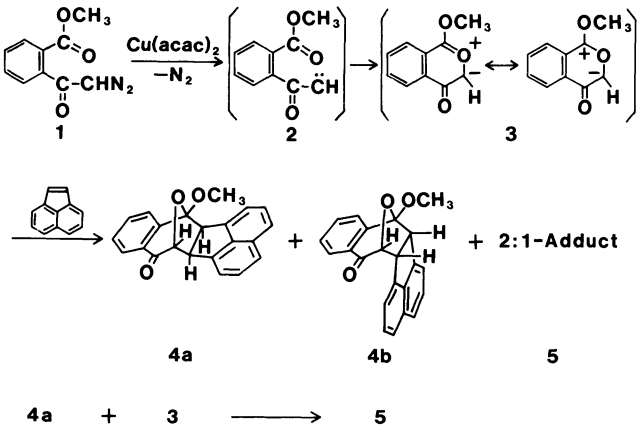
Atom	x	y	z	$B/\text{Å}^2$
H(a)	57(2)	777(2)	14(3)	1.7(5)
H(4)	77(2)	1011(2)	158(3)	3.3(6)
H(5)	−52(2)	1178(2)	284(3)	3.2(6)
H(6)	−192(2)	1151(2)	404(3)	3.5(6)
H(8)	−269(2)	1011(2)	477(3)	3.6(6)
H(9)	−270(2)	811(2)	441(3)	2.8(6)
H(10)	−141(2)	653(2)	319(3)	3.5(6)
H(b)	−6(2)	638(2)	88(3)	1.7(5)
H(c)	127(2)	616(2)	395(3)	1.4(4)
H(17)	295(2)	363(2)	2(3)	1.6(5)
H(18)	365(3)	390(3)	−198(4)	5.5(8)
H(19)	379(2)	579(2)	−202(3)	3.1(6)
H(20)	306(3)	739(2)	−29(3)	4.1(7)
H(221)	443(3)	744(2)	253(3)	4.2(8)
H(222)	419(3)	859(2)	360(4)	5.0(7)
H(223)	405(3)	763(3)	422(4)	5.4(8)
H(d)	347(2)	510(2)	462(3)	2.1(5)
H(26)	566(2)	158(2)	260(3)	3.5(6)
H(27)	523(3)	−19(2)	155(4)	4.5(7)
H(28)	311(2)	−30(2)	66(3)	3.5(6)
H(29)	158(2)	137(2)	122(3)	3.5(6)
H(321)	−62(3)	441(3)	212(4)	6.3(9)
H(322)	−70(3)	392(2)	338(4)	4.6(7)
H(323)	14(2)	478(2)	379(3)	3.2(6)

$\sum w(|F_o|-|F_c|)^2$ with the following weighting scheme: $w=1/(\sigma(F_o)^2+0.0063|F_o|+0.0006|F_o|^2)$. All the atomic scattering factors were taken from the "International Tables for X-ray Crystallography." The computations were carried out on an ACOS-S900 computer at the Crystallographic Research Center, Institute for Protein Research Laboratory, Osaka University using "The Universal Crystallographic Computing System-Osaka." Table 2 lists the final atomic and thermal parameters with their estimated standard deviations. The table of the best planes is deposited as Document No. 8534 at the Office of the Editor of Bull. Chem. Soc. Jpn. The bond distances and angles are given in Figs. 3 and 4. The atom numbering is also shown in these figures.

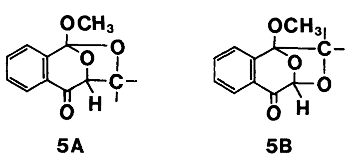
Results and Discussion

Reaction of o*-Methoxycarbonyl-α-diazoacetophenone (1) with Acenaphthylene.* The ^{1}H NMR spectrum of the 2:1-adduct (**5b**) has signals of four nonaromatic methine protons Ha, Hb, Hc, and Hd at δ 4.04 (dd), 4.39 (dt), 4.67 (d), and 5.19 (s), respectively.

The coupling patterns of protons Ha, Hb, and Hc are quite similar to those of methine protons of *exo*-1:1-adduct (**4a**).[3] This means that each pair of protons Ha–Hb and Hb–Hc locates on adjacent carbons in a similar stereochemistry observed in **4a** and that Hd is on a carbon having no vicinal proton. Therefore the 2:1-adduct is assumed to be the 1,3-dipolar cycloadduct of **3** on carbonyl group of *exo*-1:1-adduct (**4a**). This assumption was confirmed by the fact that the yield of **5b** decreased to 3% with the increase of the yields of **4a** and **4b** (25 and 34%, respectively) when 10 molar excess



Scheme 1.

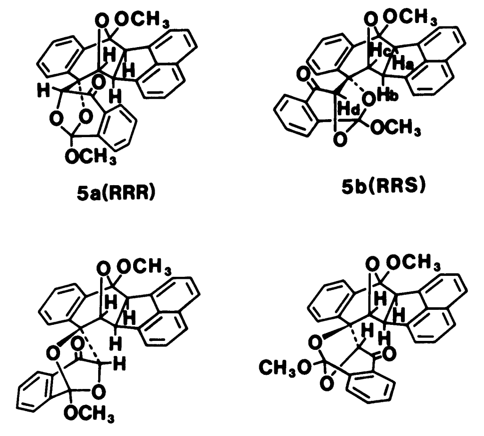


Scheme 2.

of acenaphthylene was used. The finding that the decomposition of **1** in the presence of **4a** gave the same 2:1-adduct (**5**) along with the dimers of **3**[4] is also consistent with the above consideration. On the other hand, the reaction of **3** with *endo*-1:1-adduct (**4b**) in a similar procedure did not give the 2:1-adduct but gave dimers of **3**. This indicates the poor 1,3-dipolarophilicity of the *endo*-1:1-adduct toward **3** in comparison with the reactivity of the *exo*-1:1-adduct (**4a**).

The reaction site of the 1:1-adduct (**4a**) in this reaction is assumed to be carbonyl group.[2,5] The CPK model of **4a** and **4b** reveals that the *endo*-adduct (**4b**) does not allow the approach of the carbonyl ylide (**3**) to the carbonyl group of **4b** due to the structural crowdedness caused by adjacent *o*-phenylene and acenaphthenylene groups.

In general, two regio-isomers (**5A** and **5B**) are possible in the cycloaddition of the carbonyl ylide (**3**) with carbonyl compounds. Of these, **5A** agrees with the ^{13}C NMR spectrum which shows a signal of quartanary carbon (C_{31}) of orthocarboxylate, at very low field (119.82 ppm). Four stereoisomers (**5a**—**d**) and their enantiomers are feasible in the **5A**-type adducts as is shown in Fig. 1. The stereoisomers **5a**, **5b**, **5c**, and **5d** are described as *RRR*, *RRS*, *RSR*, and *RSS*, respectively in *R*-*S* description, depending upon the stereochemistry at C_{14}, C_{15}, and C_{23}. The isomers **5a** (*RRR*) and **5b** (*RRS*) have the same stereochemistry at both C_{14} and C_{15}, but different at C_{23}. The **5c** (*RSR*) and **5d** (*RSS*) are also in the same relationship. The isomers **5a** (*RRR*) and **5c** (*RSR*) have the same



5a(RRR) **5b(RRS)**

5c(RSR) **5d(RSS)**

Fig. 1. Possible structures of the 2:1-adduct (**5**).

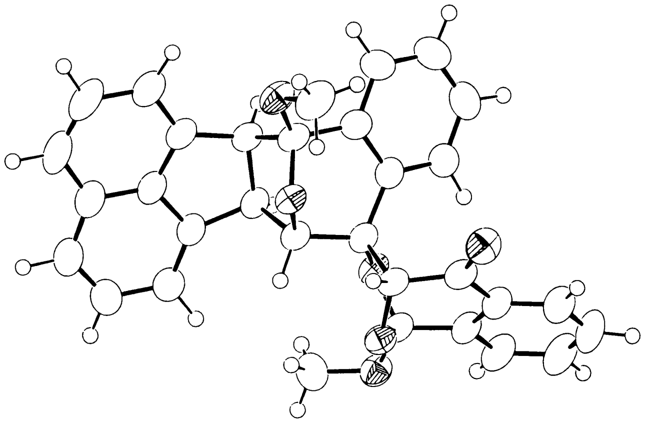


Fig. 2. Stereodrawing of the 2:1-adduct (**5b**).

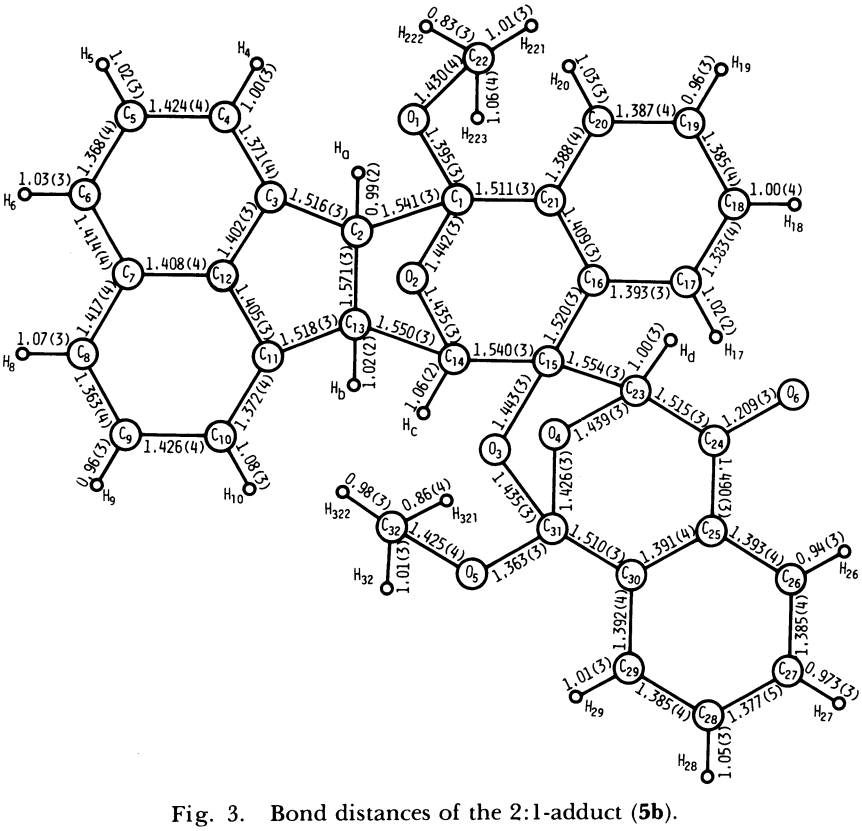
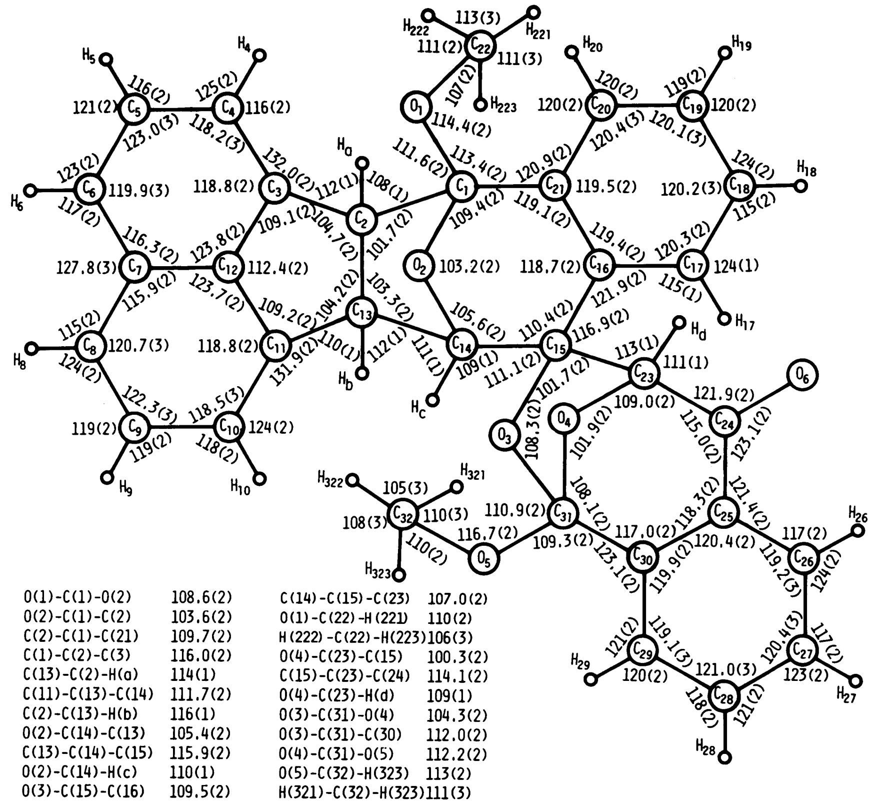


Fig. 3. Bond distances of the 2:1-adduct (**5b**).



O(1)-C(1)-O(2)	108.6(2)	C(14)-C(15)-C(23)	107.0(2)
O(2)-C(1)-C(2)	103.6(2)	O(1)-C(22)-H(221)	110(2)
C(2)-C(1)-C(21)	109.7(2)	H(222)-C(22)-H(223)	106(3)
C(1)-C(2)-C(3)	116.0(2)	O(4)-C(23)-C(15)	100.3(2)
C(13)-C(2)-H(a)	114(1)	C(15)-C(23)-C(24)	114.1(2)
C(11)-C(13)-C(14)	111.7(2)	O(4)-C(23)-H(d)	109(1)
C(2)-C(13)-H(b)	116(1)	O(3)-C(31)-O(4)	104.3(2)
O(2)-C(14)-C(13)	105.4(2)	O(3)-C(31)-C(30)	112.0(2)
C(13)-C(14)-C(15)	115.9(2)	O(4)-C(31)-O(5)	112.2(2)
O(2)-C(14)-H(c)	110(1)	O(5)-C(32)-H(323)	113(2)
O(3)-C(15)-C(16)	109.5(2)	H(321)-C(32)-H(323)	111(3)

Fig. 4. Bond angles of the 2:1-adduct (**5b**).

stereochemistry at C_{14} and C_{23}, but different at C_{15}. In these isomers the stereochemistry at C_{31} is prescribed by that at C_{23}. Therefore, there is no need to describe the stereochemistry at C_{31}.

Molecular Structure. The molecular structure of **5** determined by the X-ray analysis is given in Figs. 2—4. The results indicate that **5** has the *RRS*-structure (**5b**), which is one of the four possible structures deduced from the NMR data. The CPK-model inspection shows that the approach of **3** to the carbonyl group of the *exo*-1:1-adduct (**4a**) in the manner to give **5b** is that of the most favorable in stereochemistry. The present compound has two benzene-fused bicyclo[3.2.1]-ring systems, 8-oxabicyclo[3.2.1]-2-octene and 7,8-dioxabicyclo[3.2.1]octa-2-ene-4-one, which are combined in spiro form. Their corresponding dihedral angles are similar to each other as shown in the deposited Table. This conformation is also similar to that of the *exo*-adduct (**6**) between **3** and *N*-methylmaleimide.⁷⁾ The bond distances and angles of the 2:1-adduct (**5b**) except the C(2)-C(13) bond distance are comparable to those of **6**. The C(2)-C(13) bond distance, 1.571 Å, in the acenaphthene ring of **5b**, is considerably longer than the corresponding one (1.545 Å) of the acenaphthene-chloranile molecular complex,⁸⁾ while the bond distance is comparable to the corresponding ones (1.567, 1.562 Å) of the *cis*-dimer of acenaphthylene.⁹⁾ Two of the intramolecular distances (O···H) between the bridged oxygen atoms and the methyl-hydrogen atoms are shorter than the van der Waals distance as shown in Table 3.

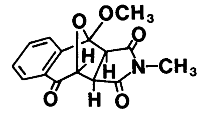


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Table 3. INTRAMOLECULAR DISTANCES BETWEEN THE BRIDGED OXYGENS AND THE METHYL HYDROGENS

O(2)···H(221)	3.24(3) Å
O(2)···H(222)	3.47(3)
O(2)···H(223)	2.36(4)
O(4)···H(321)	3.44(3)
O(4)···H(322)	3.66(3)
O(4)···H(323)	2.54(3)

Coupling Constant. In general, coupling constants of the vicinal protons depend mainly on the dihedral angles and an equation was proposed by Karplus to express the relationship between them.¹⁰⁾ The torsion angles Ha-C(2)-C(13)-Hb and Hb-C(13)-C(14)-Hc were found to be 3.8° and −97.6°, respectively, according to the present X-ray crystal structure determination. The substitution of these torsion angles in the Williamson-Johnson's equation¹¹⁾ gave calculated values of coupling constants, $J_{a,b}$=10.0 Hz and $J_{b,c}$=−0.11 Hz, which are fairly in accord with the observed values $J_{a,b}$=6.7 Hz and $J_{b,c}$=1.3 Hz.

The coupling between ^{13}C and H separating by three bonds has recently been reported to be useful for the determination of conformation of rigid cyclic systems[12] and an equation (Eq. 1) to calculate the $J(^{13}C, H)$ using the value of the dihedral angles has been reported by Wasylishen and Schaefer.[13]

$$^{3}J(^{13}C,H) = 4.26 - 1.00 \cos\theta + 3.56 \cos 2\theta \qquad (1)$$

The coupling constants $^{3}J(^{13}C_{14}\text{-Hd}) = 4.83$ Hz and $^{3}J(^{13}C_{23}\text{-Hc}) = 3.60$ Hz calculated by application of the torsion angles, $C_{10}\text{-}C_{15}\text{-}C_{23}\text{-Hd} = 33.4°$ and $C_{23}\text{-}C_{15}\text{-}C_{14}\text{-Hc} = 43.0°$, to the equation 1 are consistent with the observed values, $^{3}J(^{13}C_{14}\text{-Hd}) = 4.96$ Hz and $^{3}J(^{13}C_{23}\text{-Hc}) = 2.76$ Hz. This also supports the structure of the 2:1-adduct (**5b**).

Anisotropic Effect of Benzene Ring. The ^{1}H NMR spectrum of the 2:1-adduct (**5b**) has a doublet signal of an aromatic proton (H_{17}) at a little higher field (δ 6.28) than the signals of the usual aromatic protons. The high field shift may be attributed to the anisotropic effect of ring current of benzene. The X-ray study indicates that the aromatic hydrogen, H_{17}, locates close to the benzene ring (C_{25}–C_{30}); the perpendicular drawn from the H_{17} to the plane of the benzene ring (C_{25}–C_{30}) has a length of 2.60 Å, and the distance from the foot of the perpendicular to the center of the benzene ring is 1.96 Å.[7] The estimation of the ring current effect according to the Johnson-Bovey's ring current effect map[14] indicates that the high field shift of H_{17} is δ 0.56 ppm. This may assign the signal at δ 6.28 to H_{17}.

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