02-9; **11**, 35042-18-3; **12**, 21258-59-3; **13**, 1904-73-0.

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Isomeric Diacetal and Dimethoxime Derivatives of Acenaphthenequinone

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The reactions of acenaphthenequinone (1) with ethylene glycol and methoxyamine were investigated. The acetalization reaction afforded the monoacetal (2), the normal diacetal (3), and the bisdioxane (4). The use of mass spectrometry to differentiate between structures **3** and **4** is outlined. The loss of $C_2H_4O_2$ from the molecular ion of **4** is diagnostic for the bisdioxane structure. The two isomeric methoximes were determined by nmr spectroscopy to have the symmetrical (**6**, *E,E*) and unsymmetrical (**8**, *E,Z*) structures.

In the course of some studies that required the protection of one or both carbonyl groups of acenaphthenequinone (1), we investigated the reaction of **1** with both ethylene glycol and methoxyamine, respectively. In each case, we were able to isolate and identify isomeric addition products, and these are the subject of this paper.

Ethylene Glycol Adducts.[1]—The condensation of an α diketone with ethylene glycol in the presence of acid, when investigated about 40 years ago, was found to give a mixture of two isomers. The structure of the products obtained with glyoxal sulfate[2] or *cis*- or *trans*-2,3-dichlorodioxane[3] and ethylene glycol was a matter of controversy until quite recently.[4,5] Of late, a renaissance of activity has taken place in this general area, both in the synthesis and the differentiation of the isomeric acetals.[6-10] We have directed our attention to the use of mass spectrometry[11] as a means of structural assignment.

The acid-catalyzed reaction of acenaphthenequinone (1) with an excess of ethylene glycol in benzene gave a tricomponent mixture that was separated by silica gel plate chromatography. The least polar component was identified as the monoacetal (2), on the basis of its ir spectrum (>C=O at 5.78 μ), elemental analysis, and mass spectrum. The low-resolution mass spectrum of **2** is shown in Figure 1. The composition of the M$^+$ at *m/e* 226 was confirmed by high-resolution techniques as $C_{14}H_{10}O_3$. The odd-electron ion at *m/e* 198, arising from the loss of the ketonic carbonyl as carbon monoxide, was ten times as abundant as the ion at *m/e* 198 resulting from the elimination of ethylene. The *m/e* 170 ion had the molecular composition $C_{11}H_6O_2$. The *m/e* 198 ion eliminated C_2H_4O to form the *m/e* 154 ion. Metastable-ion defocusing experiments[12,13] confirmed that the *m/e* 182 ion was also a precursor of the *m/e* 154 ion, although the precursor ion was present in only very small abundance. However, doubly charged ions at *m/e* 182, 154, and 126 were present. Although the elimination of carbon dioxide from the *m/e* 170 ion was expected, the double decarbonylation to form the *m/e* 142 and 114 ions was unexpected, especially since the loss of a nuclear carbon was involved. To explain this finding, we postulate that the ion resulting from the elimination of ethylene from the *m/e* 198 ion rearranged, in part, to 1,8-naphtholactone, which in turn decarbonylated in two steps to form the *m/e* 114 ion. Recently, Seibl described the fragmentation of 1,8-naphtholactone by a double decarbonylation in a similar manner.[14]

The material of intermediate polarity (mp 213.5–214°) and the most polar product (mp 147.5–148°) both analyzed satisfactorily for $C_{16}H_{14}O_4$. The mass spectrum of the low-melting isomer (3) is shown in Figure 2. Below *m/e* 200, the mass spectrum is very similar to that of the ketonic product (2). The doubly charged ions at *m/e* 182, 154, and 126 are, however, more prominent in the spectrum of **3**. As in **2**, it is believed that the *m/e* 170 ion exists as the 1,8-naphtholactone ion, from which two CO groups are eliminated successively. The *m/e* 198 ion may be formed in three different ways: (1) by loss of ethylene, followed by the elimination of carbon dioxide; (2) by loss of $C_3H_4O_2$;[15] and (3) by ring cleavage, with successive losses of $C_2H_3O\cdot$ and $CHO\cdot$. The chemical-ionization spectrum of the low-melting isomer (3) is shown in Figure 3. The base ion at *m/e* 183 was probably protonated acenaphthenequinone, which had been formed through the consecutive elimination of two C_2H_4O moieties from the protonated molecular ion (MH$^+$) at *m/e* 271. These data for the low-melting

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(15) The loss of a $C_3H_4O_2$ fragment from a 1,4 diacetal has been suggested: G. Wood and E. P. Woo, *Can. J. Chem.*, **47**, 2108 (1969).

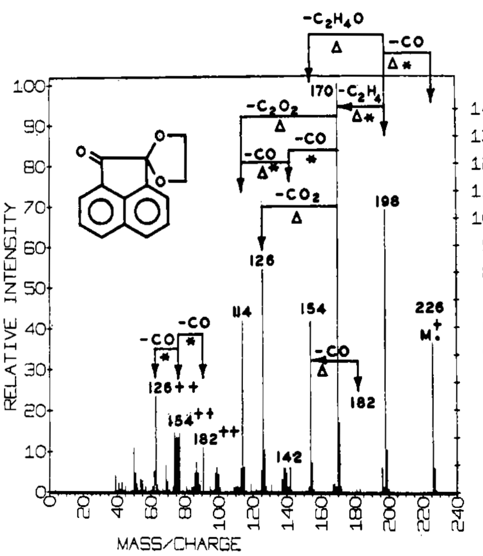


Figure 1.—Electron impact mass spectrum of 2: *, metastable transition; Δ, defocused ion transition.

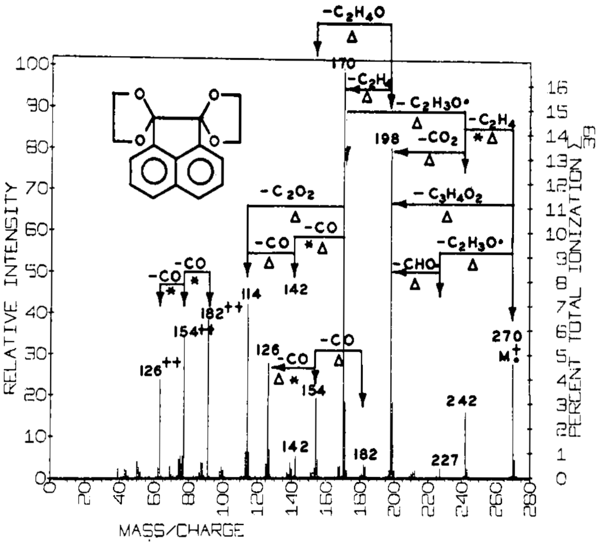
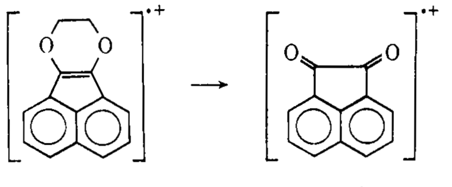


Figure 2.—Electron impact mass spectrum of 3.

isomer are consistent with the normal diacetal structure (**3**).

The mass-spectral data for the high-melting isomer are consistent only with a bisdioxane of structure **4** (Figure 4). The base ion of the latter was 16 amu lower (*m/e* 154) than in the low-melting isomer (*m/e* 170), whereas a prominent *m/e* 182 ion was observed. The *m/e* 182 ion was formed either through the elimination first of $C_2H_4O_2$ and then of ethylene, or by the reverse process; like the acenaphthenequinone ion (*cf.* Figure 5), it lost carbon monoxide in two steps. The fragmentation pathway that demonstrated the bisdioxane structure, however, was the elimination of $C_2H_4O_2$ from the molecular ion to form the stabilized unsaturated ion of *m/e* 210, which further eliminated ethylene to form the *m/e* 182 ion.[16] The $M - 58$ ion was formed by the stepwise elimination of ethylene and formaldehyde from the M^+. The ions at *m/e* 198, 170, 142, and 114 were formed in the same manner as in the low-melting isomer, *i.e.*, by the elimination of carbon dioxide from the *m/e* 242 ion. The loss of formaldehyde and $C_2H_4O_2$ could occur from a *m/e* 242 ion that had been formed from the elimination of ethylene, whereas the loss of carbon dioxide from the *m/e* 242 ion would require rearrangement to the *m/e* 198 ion present in the low-melting isomer. Although no ion was found for the loss of C_4H_8O, there were two ions at *m/e* 199, one corresponding to the ^{13}C isotope peak of the *m/e* 198 ion and the other to the loss of C_4H_7O from the M^+. In contrast to the electron impact mass spectrum of the high-melting isomer, the chemical-ionization mass spectrum (*cf.* Figure 6) shows a very intense *m/e* 199 ion. No metastable ion was detected for its formation and, unfortunately, the exact mass for this ion was not measured, nor was it determined by metastable de-



m/e 210 *m/e* 182

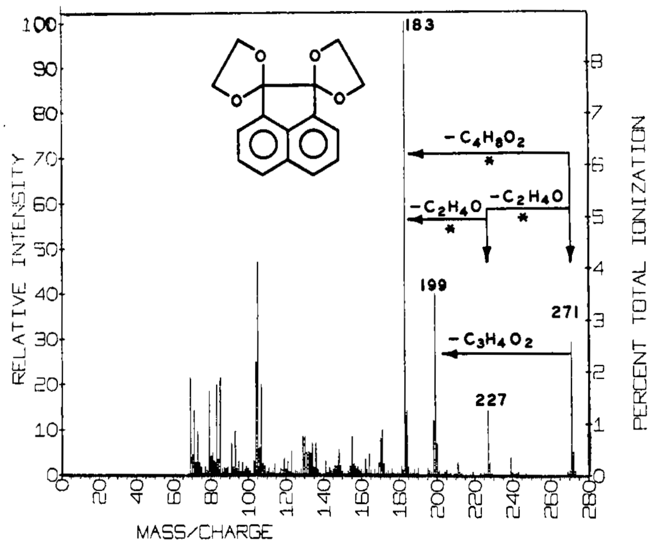


Figure 3.—Chemical ionization mass spectrum of 3.

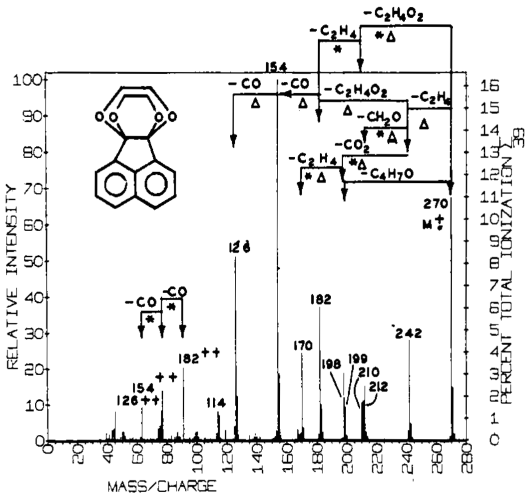


Figure 4.—Electron impact mass spectrum of 4.

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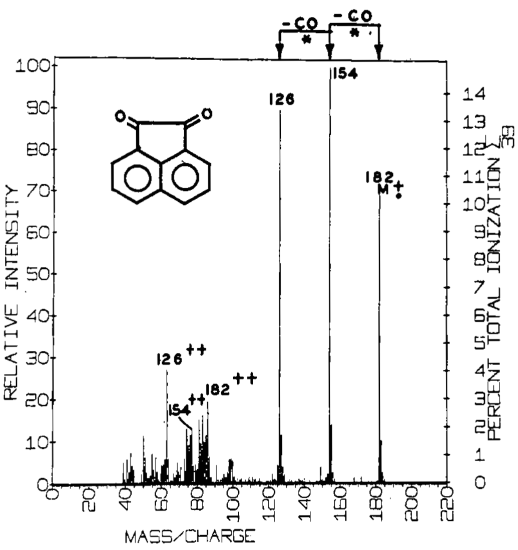


Figure 5.—Electron impact mass spectrum of **1**.

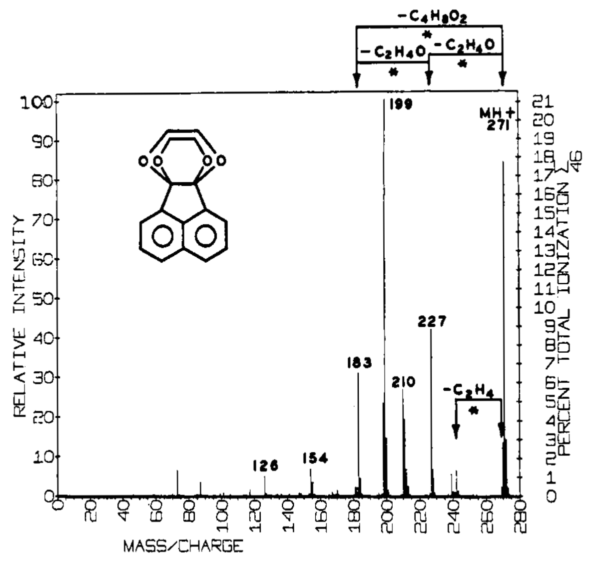


Figure 6.—Chemical ionization mass spectrum of **4**.

focusing experiments. Assuming that rearrangement is not favored in chemical ionization, C_4H_8O should be lost from the MH^+ ion to form the *m/e* 199 ion. Metastable ion transitions were observed for the consecutive losses of two C_2H_4O moieties from the MH^+. Finally, a *m/e* 210 ion was present, resulting from the elimination of $C_2H_4O_2$ and a proton to form the unsaturated ion; the ion corresponding to loss of the elements of ethylene and formaldehyde was not observed.

The reaction of cyclohexane-1,2-dione with ethylene glycol (*p*-TsOH catalysis) afforded only a small amount (~2%) of the tetraoxapropellane (**5**) along with the normal diacetal.[17] Further treatment of the normal diacetal under the same acetalization conditions did not convert it to **5**. These results are in sharp contrast to those obtained in the present case. Here, both **2** and **3** can be completely converted to **4** under further treatment, and **4** is initially formed in substantial yield. This preference for the formation of **4** is due, in part, to stabilization of a benzylic protonated intermediate. We have also examined the mass spectrum of **5** (Figure 7) and have observed the characteristic peak for the elimination of $C_2H_4O_2$ from the M^+, accompanied by both metastable and defocused ions.

Methoxyamine Adducts.—Geometrical isomerism was first observed in nitrogen compounds during the latter part of the nineteenth century, when the dioxime of benzil was shown to occur in three stereoisomeric forms. The historical aspects and chemistry of vicinal dioximes have been reviewed.[18] The dioxime of **1** has been prepared[19-22] and exists in only one form, presumably the anti[23] (*E,Z*).[24] After treatment of **1** with an excess of methoxyamine hydrochloride in pyridine, tlc and vpc of the crude crystalline product

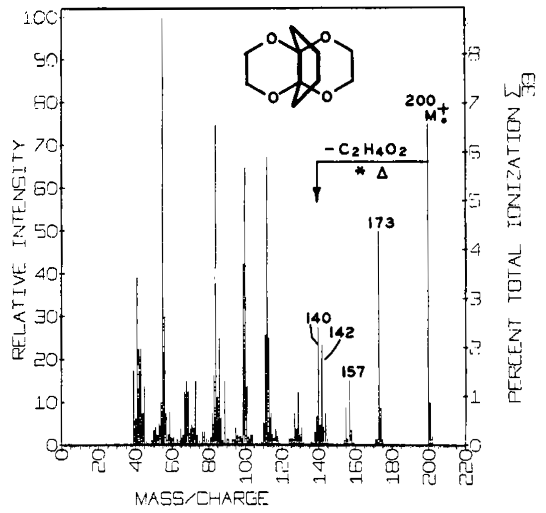
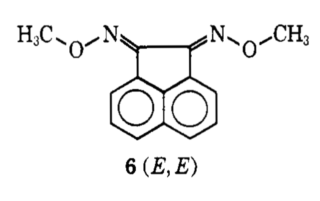
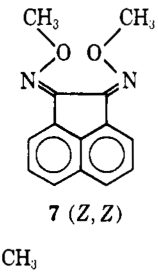


Figure 7.—Electron impact mass spectrum of **5**.

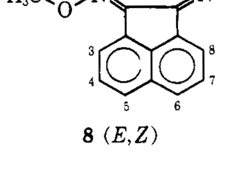
indicated the presence of two components [27% more polar isomer (A) and 73% less polar isomer (B)]. Separation of this mixture by preparative thick layer chromatography gave pure A (mp 153-153.5°) and pure B (mp 147-147.5°). There are three possible structures for the dimethoxime derivatives: two symmetrical forms [**6** (*E,E*) and **7** (*Z,Z*)] and the unsymmetrical form [**8** (*E,Z*)].



6 (*E,E*)



7 (*Z,Z*)



8 (*E,Z*)

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TABLE I

PROTON CHEMICAL SHIFTS AND COUPLING DATA OF THE DIMETHOXIMES IN DEUTERIOCHLOROFORM (HERTZ)

Compd	H-3	H-4	H-5	H-6	H-7	H-8	OCH_3
6	496.2 (q, 7.13, 0.91)	456.1 (q, 7.13, 8.01)	471.4 (q, 8.01, 0.91)	471.4 (q, 8.01, 0.91)	456.1 (q, 7.13, 8.01)	496.2 (q, 7.13, 0.91)	258.0
8	495.9 (q, 6.57, 0.72)	455.4 (q, 6.57, 7.95)	471.1 (q, 7.95, 0.72)	470.7 (q, 8.43, 0.53)	454.7 (q, 5.94, 8.43)	468.4 (q, 5.94, 0.53)	255.5, 259.2

Single methoxyl and ortho hydrogen signals were expected for **6** and **7**, owing to their symmetrical nature, whereas dual signals were expected for both the methoxyl and ortho hydrogen atoms in **8**. An inspection of the nmr data in Table I permitted the assignment of the unsymmetrical structure (**8**) to isomer A. The methoxyl signals appeared as singlets at δ 4.26 and 4.32, whereas the ortho hydrogens appeared as quartets centered at 8.26 and 7.81. It has been observed that, when an oximino oxygen atom is cis to an aromatic ring, the ortho hydrogen atom is deshielded and resonates further downfield;[24] thus, the signal at δ 8.26 was assigned to the ortho hydrogen on the side of the molecule having the methoximino group in the *E* configuration. The *E,E* configuration (**6**) was assigned to isomer B, since it exhibited a signal at δ 8.27 for both ortho hydrogens and a single methoxyl signal at 4.30. The *Z,Z* formula (**7**) was ruled out, since, in this case, the signal for the ortho hydrogens would be expected to appear further upfield at about δ 7.8. The mass spectra of **6** and **8** were identical.

Experimental Section

The melting points were determined on a Thomas-Hoover capillary apparatus and are uncorrected. The mass spectra were obtained with an AEI MS-902 double-focusing mass spectrometer (70 eV) equipped with a manually operated accelerating voltage defocusing attachment and, for high-resolution data acquisition, a Honeywell 7600 frequency-modulated analog tape recorder. The ion-block temperature was maintained at 180°. In high-resolution mode, the dynamic resolution was one part in 13,000 and the spectra were scanned at a rate of 16 sec/decade. The analog tape was processed on an IBM 1800 computer, using Squibb programs. The accuracy of high-resolution mass measurements was better than 10 ppm whereas that of metastable ion defocusing was ±1 amu. Chemical ionization spectra were obtained by Dr. H. Fales on a modified AEI MS-902, with methane at 0.5-mm pressure, 220°. The nmr spectra were determined on a Varian Associates A-60 spectrometer operated at ambient temperatures, employing TMS as the internal standard. The chemical shifts and coupling constants were calculated by use of NMREN and NMRIT[25] programs. Computed spectra from the above data gave the best fit to the experimental spectra. Average deviations were <0.16 Hz in all cases. Plate chromatography was carried out on silica gel (Quantum Industries, PQ1F, 20 × 40 cm plates) and the compounds were visualized with ultraviolet light.

Reaction of Acenaphthenequinone (1) with Ethylene Glycol.—A mixture of 1 (1.0 g) and *p*-TsOH (50 mg) in benzene (50 ml) and ethylene glycol (5 ml) was stirred and refluxed overnight in a modified Dean–Stark trap containing a calcium carbide thimble. The mixture was cooled and the benzene layer separated. The aqueous layer was diluted with H_2O and extracted with benzene. The combined benzene fractions were washed with 8% salt solution, dried (Na_2SO_4), and evaporated. Plate chromatography of the residue, using $CHCl_3$ as the developing solvent, gave rise to three bands, which were eluted with EtOAc.

The least polar product was crystallized from chloroform–isopropyl ether to give **2** (115 mg, mp 93–94°).

Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.14; H, 4.45.

The product of intermediate polarity was crystallized from chloroform–isopropyl ether to give **4** (218 mg): mp 213.5–214°; nmr ($CDCl_3$) δ 5.69 (m, OCH_2CH_2O, $w_{1/2}$ = 3 Hz).

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.85; H, 5.26.

The most polar product was crystallized from chloroform–isopropyl ether to give **3** (297 mg): mp 147.5–148°; nmr ($CDCl_3$) δ 6.03 (AA'BB' pattern, OCH_2CH_2O, w = 55 Hz).[6]

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.23; H, 5.48.

Reaction of Acenaphthenequinone (1) with Methoxyamine.—A mixture of 1 (5.0 g) and methoxyamine hydrochloride (5.0 g) in pyridine (100 ml) was warmed to achieve solution and then left at room temperature overnight. The mixture was poured into H_2O, and the solid was collected by filtration. The solid was dissolved in $CHCl_3$, and this solution was washed with 2 *N* HCl and with 8% salt solution, then dried (Na_2SO_4), and evaporated to give the mixture of dimethoximes (4.1 g, mp 124–130°). Plate chromatography of the mixture, using chloroform–hexane (1:1) as the developing solvent, gave rise to two bands, which were eluted with EtOAc.

Crystallization of the less polar product from isopropyl ether gave **6** (mp 147–147.5°).

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.70; H, 5.06; N, 11.60.

Crystallization of the more polar product from isopropyl ether gave **8** (mp 153–153.5°).

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.13; H, 5.06; N, 11.67.

Registry No.—**1**, 82-86-0; **2**, 30339-97-0; **3**, 30339-98-1; **4**, 30384-15-7; **6**, 35171-04-1; **8**, 35171-05-2.

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