

## AROMATIC NUCLEOPHILIC SUBSTITUTION—II<sup>1</sup>

### INTERMEDIATES IN THE REACTIONS OF 2,4-DINITRO-OR 2,4,5-TRINITRO-1-NAPHTHYL ETHYL ETHER WITH SECONDARY AMINES AND PREPARATION OF A SPIRO MEISENHEIMER COMPLEX

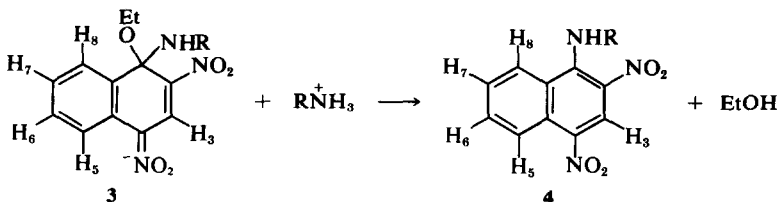
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(Received in Japan 26 May 1973; Received in the UK for publication 4 July 1973)

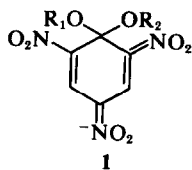
**Abstract**—The intermediates in the reactions of 2,4-dinitro-(2) or 2,4,5-trinitro-1-naphthyl ethyl ether (11) with secondary amines have been studied. In the reaction of 2 with piperidine, the NMR spectrum of the reaction system indicated the coexistence of the three species—starting material, Meisenheimer complex, and substituted product. In the reaction of 11 with piperidine or N-methyl-n-butylamine, the NMR spectra of the reaction system indicated the presence of a Meisenheimer complex, but did not indicate the formation of a substituted product. In addition, the spiro Meisenheimer complex (9) was prepared from 1-[N-methyl-(2'-hydroxy)ethylamino]-2,4,5-trinitronaphthalene (8) and sodium methoxide.

In 1900, Jackson and Gazzolo<sup>2</sup> proposed a quinoid structure<sup>3†</sup> 1, (R<sub>1</sub>, R<sub>2</sub> = alkyl) for the coloured adducts from picryl ether and potassium alkoxides, and in 1902, Meisenheimer<sup>4</sup> independently isolated

and they showed that the intermediate (3), produced in the initial stage, underwent acid-catalysed reaction with butylammonium ion to separate the alcohol. The complex 3 is considered to be the first



1 (R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>) by treating picryl methyl ether



with potassium methoxide. This adduct is generally termed a Meisenheimer complex or an anionic  $\sigma$  complex (hereinafter referred to as  $\sigma$  complex). Since then, a large number of  $\sigma$  complexes have been prepared. However, only a few polynitronaphthalene  $\sigma$  complexes have been prepared.<sup>5-9</sup> Orvik and Bunnett<sup>10</sup> studied the nucleophilic substitution reaction of 2,4-dinitronaphthyl ethyl ether (2) with *n*- or *t*-butylamine in dimethyl sulphoxide,

example of a polynitrophenylene  $\sigma$  complex, having an N—C (ring carbon)—O bond.

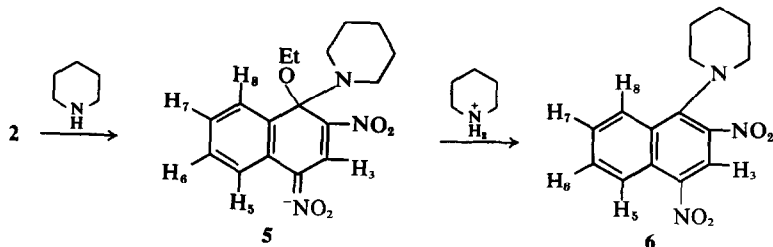
This paper reports the confirmation of the presence of complexes in the reactions of 2 or 11 with piperidine or N-methyl-n-butylamine in dimethyl sulphoxide.<sup>11</sup>

#### RESULTS AND DISCUSSION

**Reaction of 2,4-dinitro-1-naphthyl ethyl ether (2) with piperidine.** The addition of excess piperidine to a solution of 2 in DMSO (piperidine 1.0 mole/l, 2  $2.87 \times 10^{-5}$  mole/l) gave a red species ( $\lambda_{\max}$  357, 365, and 524 nm).<sup>11</sup> The optical density at 365 nm is about one-half that at 524 nm. Not only the shapes, but also the positions and intensities of these bands are similar to those of 1,1-disubstituted polynitronaphthalene  $\sigma$  complexes.<sup>3e</sup> Therefore, from the work of Orvik and Bunnett<sup>10</sup> this reaction process is formulated as follows:

As a result, when the complex 5 is relatively

<sup>†</sup>Molecular orbital calculations and crystal-structure determinations indicate that most of the negative charge is located on the NO<sub>2</sub> group *para* to the sp<sup>3</sup> ring carbon.<sup>3</sup>



stable, three species **2**, **5** and **6** are expected to coexist in the reaction system.

The NMR spectra of the system are shown in Fig 1. After excess piperidine ( $2.83 \times 10^{-3}$  mole) had been added to **2** ( $1.91 \times 10^{-4}$  mole) in DMSO (0.26 ml), the  $H_3$  band intensity of **2** ( $\delta$  8.83, Fig 1A, 1B) immediately decreased and, at the same time, its band position was shifted to  $\delta$  9.18, attributed to  $H_3$  of **5**,<sup>1,5a</sup> and a new singlet appeared at  $\delta$  8.62, attributed to  $H_3$  of **6** (Fig 1B, 1D). In Fig 1B, the broad band appeared at about  $\delta$  7.35, attributed to  $H_6$  and  $H_7$  of **5**.<sup>1,5</sup> From the calculation of band intensity, the  $H_5$  band of **5** was found to overlap with the  $H_6$  and  $H_7$  bands (multiplet,  $\delta$  7.92) of **6**, and the  $H_6$  band of **5** was found to overlap with the  $H_3$  band (s,  $\delta$  8.60) of **6**, as well as the  $H_5$  and  $H_8$  bands (m,  $\delta$

8.50) of **2**. With time the bands, attributed to the aromatic protons of **5** decreased in intensity while the bands attributed to the protons of **6** increased in intensity (Fig 1C). Finally, the spectrum of the reaction system agreed with that of **6** (Fig 1D). That the spectra represent attack of piperidine at C-3 is denied, because a marked upfield shift of the  $H_3$  band of **7** is not observed.<sup>5a,12</sup>

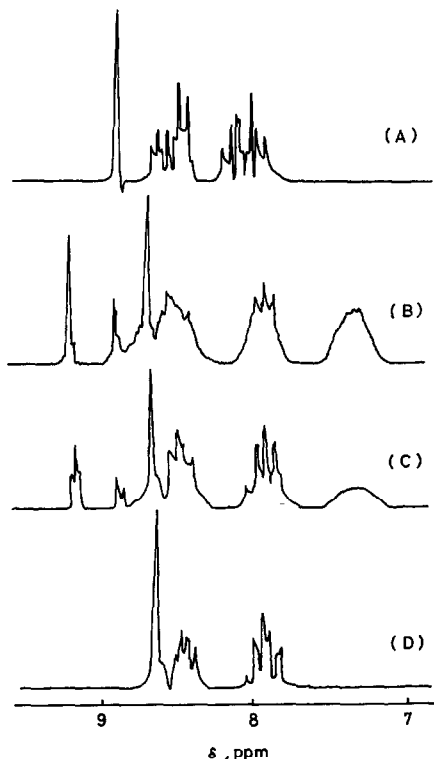
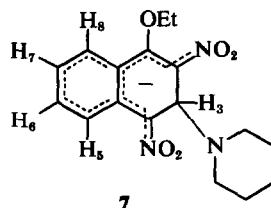


Fig 1. NMR spectra relevant of the reaction of **2** with piperidine: (A) **5** before addition of piperidine; (B), (C), and (D) ca. 8, 20, and 180 min, respectively, after addition of piperidine.

*Preparation of a spiro  $\sigma$  complex (9) from 1-[N-methyl-(2'-hydroxy)-ethylamino]-2, 4, 5-trinitronaphthalene (8) and sodium methoxide.* In previous work<sup>1</sup> we were successful in preparing a spiro  $\sigma$  complex (**10**) containing an N—C (ring carbon)—O bond from 1-[N-methyl-(2'-hydroxy)ethylamino]-2,4-dinitronaphthalene and sodium methoxide. As a reference compound for work described in the next paragraph, a spiro  $\sigma$  complex (**9**) was prepared from **8** and sodium methoxide according to the method described in the previous paper.<sup>1</sup> The visible spectrum of **9** in DMSO ( $\lambda_{max}$  366 and 499 nm) was very similar to that of **10** in shapes, positions, and intensities. The NMR spectral data are shown in Fig. 2. The downfield shift ( $\delta$  7.75  $\rightarrow$  8.85) of the  $H_3$  band and upfield shifts of the  $H_6$  ( $\delta$  9.03  $\rightarrow$  7.75),  $H_8$  ( $\delta$  8.58  $\rightarrow$  7.75), and  $H_7$  ( $\delta$  7.96  $\rightarrow$  7.27) bands of **8** in the conversion of **8** to **9** were similar to those in the conversion of **2** to **5**. Moreover, the chemical shifts of the aromatic proton bands of **9** were similar to those of the 1,1-dimethoxy-substituted 2,4,5-trinitronaphthalene  $\sigma$  complex.<sup>13</sup> These results indicated the structure of this complex to be **9**. This structure is also supported by the absence of an  $H^p$  band.

*Reaction of 2,4,5-trinitro-1-naphthyl ethyl ether (11) with piperidine or N-methyl-n-butylamine (NMBA).* As in the reaction of **2** with piperidine, the addition of excess piperidine or NMBA to a solution of **11** in DMSO (in the former case, piperidine 0.2 mole/l, **11**  $2.2 \times 10^{-4}$  mole/l; in the latter case, NMBA 0.38 mole/l, **11**  $3.39 \times 10^{-4}$  mole/l) gave red

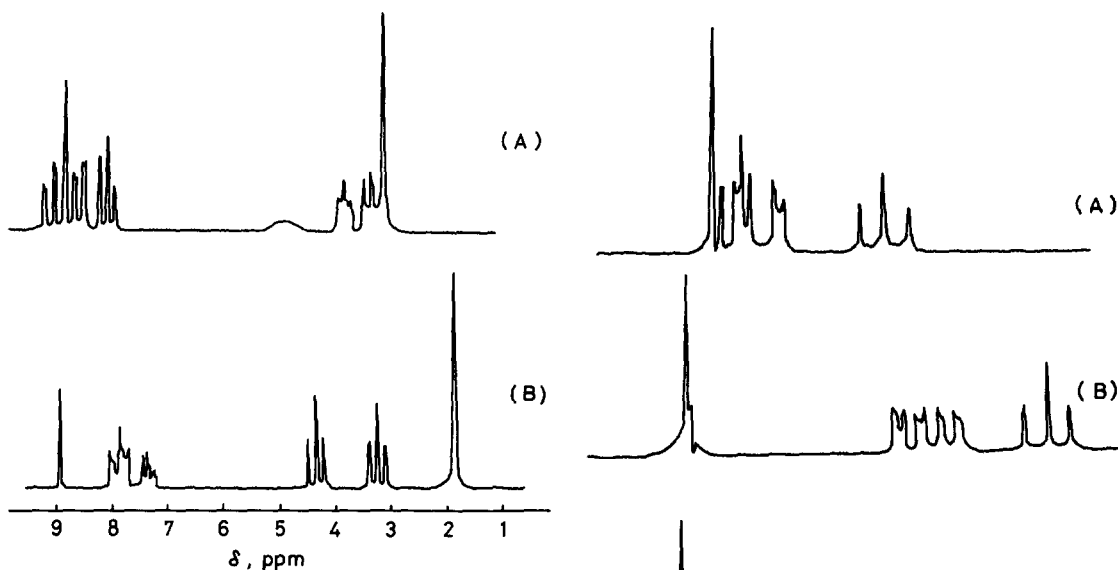
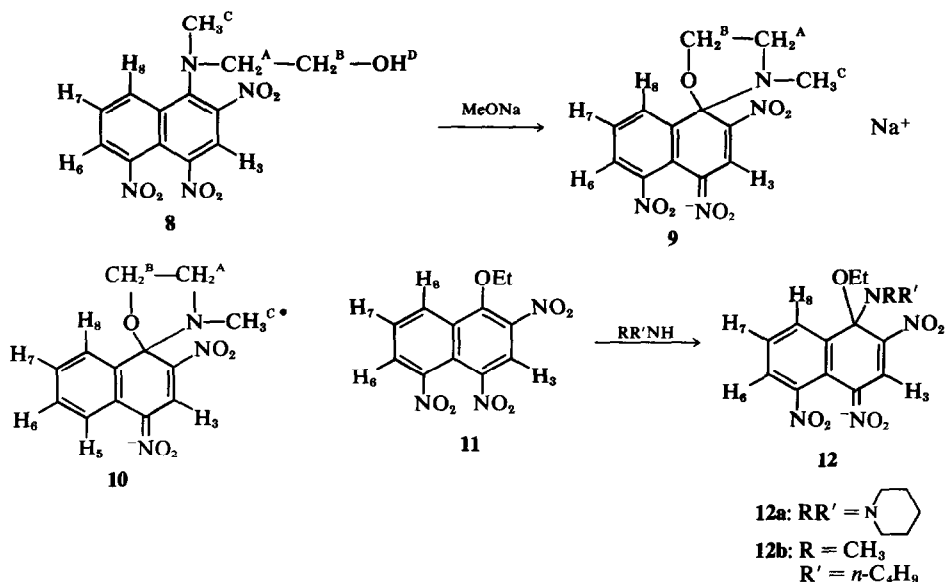


Fig 2. NMR spectra of 8(A) and 9(B).

species (in the former case,  $\lambda_{\text{max}}$  505 and 350 nm; in the latter case,  $\lambda_{\text{max}}$  503 and 350 nm).

The shapes, positions, and intensities of the bands in their visible spectra were similar to those in the reaction of 2 with piperidine. The NMR spectra of the reaction systems are shown in Fig 3. In Fig 3A, the  $\text{H}_3$ ,  $\text{H}_6$ ,  $\text{H}_8$ , and  $\text{H}_7$  bands of 11 appeared at  $\delta$  8.96, 8.85, 8.68, and 8.08, respectively, and, further, the  $\text{H}_6$  and  $\text{H}_8$  bands were split into two lines, with a coupling constant ( $J = 2$  Hz). When 11 was changed into 12, the  $\text{H}_3$  band was shifted downfield ( $\delta$  9.08 for 12a;  $\delta$  9.10 for 12b), and the  $\text{H}_6$ ,  $\text{H}_8$ , and  $\text{H}_7$  bands were shifted upfield ( $\delta$  7.97, 7.73, 7.23 for 12a;  $\delta$  7.99, 7.73, 7.27 for 12b). These shifts are

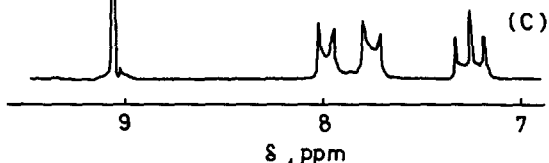
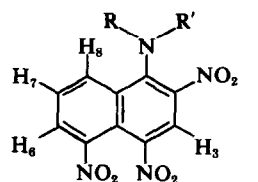


Fig 3. NMR spectra relevant of the reaction of 11 with secondary amines: (A) 11 before addition of amine; (B) immediately after addition of piperidine; (C) immediately after addition of N-methyl-n-butylamine.

characteristic of a 1,1-disubstituted 2,4,5-trinitrophenyl  $\sigma$  complex.<sup>5</sup> The chemical shifts of the aromatic protons of 12a and 12b are very similar to

those of **9**, indicating the formation of 1,1-disubstituted  $\sigma$  complexes. Although **12** decomposed with time, the spectra did not contain bands expected for the substitution product (**13**), but became very complex. Study of the decomposition process



**13a:** RR' =   
**13b:** R = CH<sub>3</sub>, R' = n-C<sub>4</sub>H<sub>9</sub>

H<sub>8</sub>), 7.92 (m, 2H, —H<sub>6</sub>, H<sub>7</sub>). (Found: C, 59.80; H, 4.98%. C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>4</sub> requires: C, 59.79; H, 5.02%).

**Preparation of 1-[N-methyl-(2'-hydroxy)ethylamino]-2,4,5-trinitronaphthalene (8).** To a stirred soln of 1-chloro-2,4,5-trinitronaphthalene (6.0 g, 0.02 mole) in acetone (50 ml) was added a soln of N-methylethanolamine (3.2 g, 0.043 mole) in acetone (50 ml). After the mixture had been stirred for 4 hr, it was poured into ice water (300 ml), extracted with chloroform, washed with a 2% Na<sub>2</sub>CO<sub>3</sub> aq, and dried. Evaporation of the solvent gave the crude **8** quantitatively. As the crude product was difficult to recrystallize, the product purified by column chromatography on silica gel (benzene-acetone) was used for the preparation of **9**. NMR (DMSO-d<sub>6</sub>):  $\delta$  8.77 (s, 1H, —H<sub>3</sub>), 9.03 (d, 1H, —H<sub>6</sub>), 8.58 (d, 1H, —H<sub>8</sub>), 7.96 (t, 1H, —H<sub>7</sub>), 3.29 (t, 2H, —H<sup>A</sup>), 3.74 (t, 2H, —H<sup>B</sup>), 3.14 (s, 3H, —H<sup>C</sup>), and 4.73 (s, 1H, —H<sup>D</sup>).

**Preparation of a spiro  $\sigma$  complex (9).** The mixture of **8**

Table 1. NMR spectral data for complexes<sup>a</sup>

Compound	H <sub>3</sub>	H <sub>8</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sup>B</sup>	H <sup>A</sup>	H <sup>C</sup>
<b>5</b>	9.18 (s)	— <sup>b</sup>	— <sup>b</sup>	7.35 <sup>c</sup>	—	—	—	—
<b>9</b>	8.85 (s)	7.75 (m)	—	7.75 (m)	7.27 (t)	4.34 (t)	3.29 (t)	1.90 (s)
<b>12a</b>	9.08 (s)	7.73 (d)	—	7.97 (d)	7.23 (t)	—	—	—
<b>12b</b>	9.10 (s)	7.73 (d)	—	7.99 (d)	7.27 (t)	—	—	—

<sup>a</sup>All spectra are recorded in DMSO-d<sub>6</sub> at 25°. Chemical shifts are given on  $\delta$  scale relative to internal TMS.

<sup>b</sup>H<sub>8</sub> band overlapped with H<sub>3</sub> band of **6** and H<sub>5</sub> and H<sub>6</sub> bands of **2**. H<sub>5</sub> band overlapped with H<sub>6</sub> and H<sub>7</sub> bands of **6**.

<sup>c</sup>Broad band.

after the formation of the  $\sigma$  complex is now in progress. For completeness all NMR spectral data for the complexes are included in Table 1.

#### EXPERIMENTAL

Capillary m.ps are uncorrected. NMR spectra were recorded with a Varian A-60D spectrometer. Elemental analyses were performed at the Microanalytical Center of Gunma University. Visible spectra were measured with a Hitachi-124 UV-VIS spectrophotometer.

**Preparation of 2,4-dinitro-1-naphthyl ethyl ether (2).** This compound was prepared according to the method of Ullman and Bruck,<sup>14</sup> m.p. 91–92° (91°).<sup>14</sup> NMR (DMSO-d<sub>6</sub>):  $\delta$  8.83 (s, 1H, —H<sub>3</sub>), 8.50 (m, 2H, —H<sub>5</sub>, H<sub>8</sub>), 8.02 (m, 2H, —H<sub>6</sub>, H<sub>7</sub>).

**Preparation of 2,4,5-trinitro-1-naphthyl ethyl ether (11).** To a refluxing soln of 1-chloro-2,4,5-trinitronaphthalene (2 g, 6.7 × 10<sup>-3</sup> mole) in EtOH (160 ml) was added ethanolic NaOEt (Na 0.17 g in 30 ml EtOH) in small portions under stirring. After an additional 15 min's refluxing, the mixture was cooled, and poured into excess water. Recrystallization of the ppt formed from EtOH gave 1.2 g (58.2%) of an analytical sample, m.p. 148–149°. NMR (DMSO-d<sub>6</sub>):  $\delta$  8.96 (s, 1H, —H<sub>3</sub>), 8.85 (d, 1H, —H<sub>6</sub>), 8.68 (d, 1H, —H<sub>8</sub>), 8.08 (t, 1H, —H<sub>7</sub>). (Found: C, 46.87; H, 3.06%. C<sub>17</sub>H<sub>9</sub>N<sub>3</sub>O<sub>7</sub> requires: C, 46.92; H, 2.95%).

**Preparation of 1-(N-piperidyl)-2,4-dinitronaphthalene (6).** To a stirred soln of 1-chloro-2,4-dinitronaphthalene (1.5 g, 5.0 × 10<sup>-3</sup> mole) in DMSO (50 ml) was added piperidine (1.00 ml, 0.01 mole). The mixture was stirred at 40–45° for 8.5 hr, and then poured into a large amount of water, filtered, and dried. Recrystallization from EtOH gave an analytical sample quantitatively, m.p. 136–137°. NMR (DMSO-d<sub>6</sub>):  $\delta$  8.60 (s, 1H, —H<sub>3</sub>), 8.47 (m, 2H, —H<sub>5</sub>,

(0.52 g, 1.55 × 10<sup>-3</sup> mole) in DMSO (5 ml) and 0.34 ml (0.95 × 10<sup>-3</sup> mole) methanolic NaOMe (4.34 mole/l) was stirred for 1 hr. The mixture was poured into a mixed solvent (50 ml) of benzene and cyclohexane (1:1). The ppt was washed with this mixed solvent, and, then, with diethyl ether, and dried, yield 0.47 g (84.8%). NMR (DMSO-d<sub>6</sub>):  $\delta$  8.85 (s, 1H, —H<sub>3</sub>), 7.75 (m, 2H, —H<sub>6</sub>, H<sub>8</sub>), 7.27 (t, 1H, —H<sub>7</sub>), 3.29 (t, 2H, —H<sup>A</sup>), 4.34 (t, 2H, —H<sup>B</sup>), 1.90 (s, 3H, —H<sup>C</sup>). (Found: C, 43.67; H, 3.30. C<sub>13</sub>H<sub>11</sub>N<sub>4</sub>O<sub>7</sub>Na requires: C, 43.59; H, 3.10%).

**Preparation of 1-(N-piperidyl)-2, 4, 5-trinitronaphthalene (13a).** To a stirred soln of 1-chloro-2,4,5-trinitronaphthalene (1.5 g, 0.005 mole) in DMSO (20 ml) was dropwise added piperidine (0.86 g, 0.01 mole) at room temp. Then, the mixture was allowed to stand for a day, poured into excess water, filtered, and dried. Recrystallization of the ppt from glacial AcOH gave an analytical sample quantitatively, m.p. 194–195°. NMR (DMSO-d<sub>6</sub>):  $\delta$  8.77 (s, 1H, —H<sub>3</sub>), 8.77 (d, 1H, —H<sub>6</sub>), 8.65 (d, 1H, —H<sub>8</sub>), 8.05 (t, 1H, H<sub>7</sub>). (Found: C, 51.81; H, 3.99. C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>O<sub>6</sub> requires: C, 52.03; H, 4.08%).

Compound **13b** was prepared by the similar method. Recrystallization from MeOH gave an analytical sample quantitatively, m.p. 104–105°. NMR (DMSO-d<sub>6</sub>):  $\delta$  8.77 (s, 1H, —H<sub>3</sub>), 8.82 (d, 1H, —H<sub>6</sub>), 8.58 (d, 1H, —H<sub>8</sub>), 8.02 (t, 1H, —H<sub>7</sub>). (Found: C, 51.79; H, 4.54. C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O<sub>6</sub> requires: C, 51.72; H, 4.63%).

**NMR measurement.** A certain amount of a sample (ca 35 mg) was dissolved in a small amount of DMSO (ca 0.25 ml) in a NMR tube. After excess amine (ca 200  $\mu$ l) had been added in the soln through a microsyringe and shaken vigorously, the mixture was measured.

**Acknowledgement**—We thank the Asahi Glass Foundation for the Contribution to Industrial Technology for

their financial support. We wish to thank Professor J. F. Bunnett, the University of California, Santa Cruz, for criticism of the manuscript.

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