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Two-dimensional ^{1}H-, ^{13}C- and ^{15}N-NMR Spectra of Azo Dyes Derived from J-Acid, H-Acid and Gamma Acid*

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SUMMARY

The ^{1}H-, ^{13}C- and ^{15}N-NMR spectra of compounds prepared by coupling benzenediazonium chloride with J-acid, H-acid and Gamma acid under alkaline conditions have been measured. Two-dimensional H,H-COSY, NOESY, H,C-COSY and COLOC spectra and one-dimensional selective INEPT have been used in the assignment of the ^{1}H- and ^{13}C-NMR signals. The results show that the above-mentioned aminohydroxynaphthalenesulfonic acids undergo diazo coupling of benzenediazonium chloride ortho to the hydroxyl groups under alkaline conditions. Using $\delta(^{13}C)$, $\delta(^{15}N)$ and $^{1}J(^{15}NH)$ it has been found that the coupling products exist, in hexadeuteriodimethyl sulfoxide solutions, as equilibrium mixtures of the azo and hydrazone tautomers with strongly prevailing naphthoquinone phenylhydrazone configurations.

1 INTRODUCTION

It has been generally accepted for many years[1–3] that aminohydroxynaphthalenesulfonic acids (J-, H- and Gamma acids) undergo diazo coupling of benzenediazonium chloride *ortho* to the hydroxyl group at pH > 8. Recently a paper has been published[4] in which it is stated that J-acid and H-acid undergo diazo coupling exclusively *para* to the hydroxyl group under alkaline conditions. The determination of the structures of these dyes with the aid of ^{1}H-NMR spectroscopy was described in this paper.

* Dedicated to Dr V. Štěrba on the occasion of his 65th birthday.

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Azo dyes can exist as azo compounds or hydrazone compounds or their mixtures.[5] Diazo coupling products with aminohydroxynaphthalenesulfonic acids are mostly formulated only as azo compounds[3] or azo–hydrazone tautomerism is consciously omitted.[6] Fedorov *et al.* have observed that monoazo dyes[7] derived from chromotropic acid (4,5-dihydroxy-2,7-naphthalenedisulfonic acid) exist exclusively in the hydrazone form while bisazo dyes[8] are in the azo configuration.

The aim of this communication is to judge the coupling position of benzenediazonium chloride with J-, H- and Gamma acids under alkaline conditions using two-dimensional ^{1}H- and ^{13}C-NMR spectra and to interpret ^{13}C- and ^{15}N-NMR spectra in the above-mentioned compounds with respect to azo–hydrazone tautomerism.

2 EXPERIMENTAL

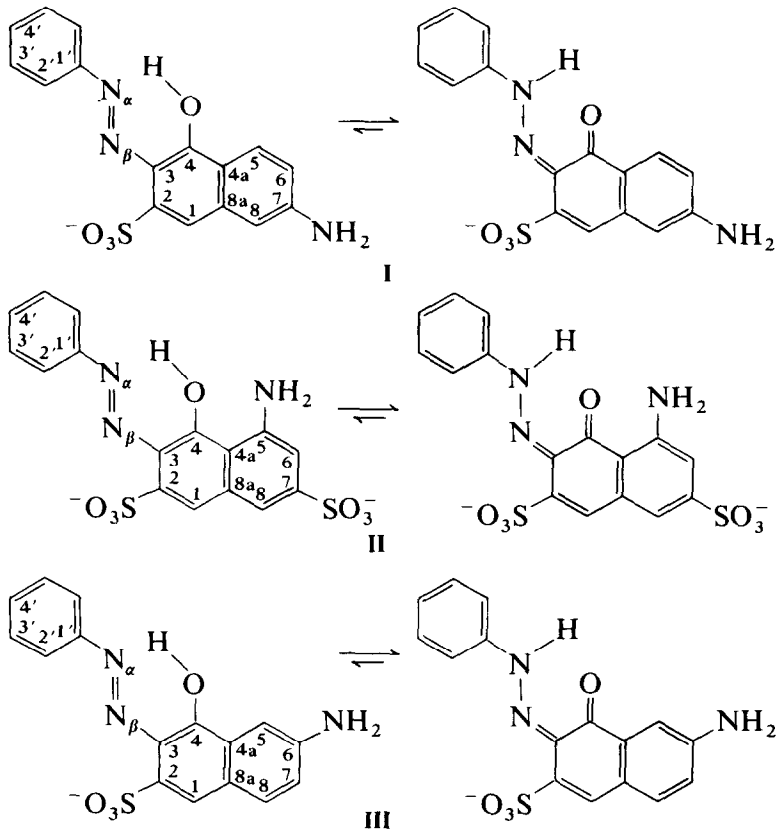
Sodium salts of 7-amino-4-hydroxy-3-phenylazo-2-naphthalenesulfonic acid (**I**), 5-amino-4-hydroxy-3-phenylazo-2,7-naphthalenedisulfonic acid (**II**) and 6-amino-4-hydroxy-3-phenylazo-2-naphthalenesulfonic acid (**III**) (Scheme 1) were prepared according to ref. 4 under alkaline conditions. ^{15}N-labelled compounds were prepared with [^{15}N]aniline (15% or 95% ^{15}N) and $Na^{15}NO_2$ (96·2% ^{15}N; Isocommerz, Berlin).

^{1}H- and ^{13}C-NMR spectra were measured at 400·13 and 100·61 MHz, respectively, using an AM 400 (Bruker) spectrometer. The spectra were recorded for saturated solutions in hexadeuteriodimethyl sulfoxide. The deuterated solvent was used as a lock substance. The ^{1}H and ^{13}C chemical shifts were referenced to the signal of solvent ($\delta(^{1}H) = 2{\cdot}55$, $\delta(^{13}C) = 39{\cdot}6$). The measurement conditions were as follows:

(a) H,H-COSY (COSY[9]): 5-mm tube, relaxation time 2 s, $90°(^{1}H) = 10{\cdot}5\ \mu s$, 90° mixing pulse, $F_1 = F_2 = 620$ Hz, data matrix 1024 × 512, eight scans during 256 time increments (zero filling in F_1), two dummy scans, sine-bell multiplication in both dimensions. Spectra were symmetrized.

(b) 2D NOE (NOESY[9]): 5-mm tube, relaxation time 4 s, $F_1 = F_2 = 620$ Hz, mixing time 0·8 s ± 5%, data matrix 512 × 256, 16 scans, sine-bell multiplication in both dimensions. Spectra were symmetrized.

(c) H,C-COSY (XHCORRC[9]): 10-mm tube, relaxation time 2 s, $90°(^{1}H) = 9{\cdot}7\ \mu s$, $90°(^{13}C) = 8{\cdot}5\ \mu s$, polarization time = refocusing time = 3·1 ms, $F_1 = 620$ Hz, $F_2 = 2300$ Hz, data matrix 1024 × 256, from 8 to 32 scans during 128 time increments (zero filling in F_1), two



Scheme 1

dummy scans, Gaussian multiplication in F_1, sine-bell (shifted $\pi/5$) multiplication in F_2.

(d) COLOC (COLOC[9]): 10-mm tube, relaxation time 1·5 s, $\Delta_1 = 51$ ms, $\Delta_2 = 31$ ms, $F_1 = 620$ Hz, $F_2 = 6850$ Hz, data matrix 2048 × 128, 64 scans during 64 time increments (zero filling in F_1), two dummy scans, Gaussian multiplication in both dimensions.

(e) The selective INEPT spectra were measured according to ref. 10 (number of scans 500–2000).

^{15}N-NMR spectra of ^{15}N-labelled dyes **I–III** were measured at 10·095 MHz using a JNM-FX 100 (JEOL) spectrometer equipped with a multinuclear tunable probe and operating in the FT mode. The ^{15}N chemical shifts were referenced to external neat nitromethane (25% ^{15}N, $\delta = 0{\cdot}0$). The temperature of the heating gas was measured with a thermocouple with an accuracy of ± 1 K. The measurement conditions are given in ref. 11.

3 RESULTS AND DISCUSSION

The ^{1}H-NMR spectra of dyes **I–III** measured in hexadeuteriodimethyl sulfoxide[12] are characterized by a one-proton singlet at very low field (δ = 15·5–16·2) which was attributed[4] to the increased acidity of the aromatic hydroxyl group proton *ortho* (**III**) or *para* (**I**; **II**) to the strongly electron-withdrawing azo moiety. We believe that this interpretation is incorrect because in 2,4-dinitro-1-naphthol (Naphthol Yellow) containing two substituents having much more electron-withdrawing character we have observed δ(OH) = 12·48 in deuteriochloroform, whilst in hexadeuteriodimethyl sulfoxide (used without special drying) we have found one common signal with traces of water from solvent, shifted upfield with respect to aromatic ^{1}H-NMR signals. Very low field signals (δ = 15·5–16·2) are typical of azo hydrazone tautomerism.[13]

We believe that J-, H- and Gamma acids undergo diazo coupling of benzenediazonium chloride *ortho* to the hydroxyl groups under alkaline conditions. We have used ^{1}H and ^{13}C two-dimensional[14–16] NMR spectra for the corroboration of the above-mentioned assumption. Out of more than 100 pulse sequences[16] we chose homonuclear shift-COrrelated

TABLE 1
^{1}H and ^{13}C Chemical Shifts and Coupling Constants $^nJ(^{15}N_\beta{}^{13}C)$ of Compound **I** in Hexadeuteriodimethyl Sulfoxide at 300 K

H/C number	$\delta(^1H)$[a]	$\delta(^{13}C)$	$^nJ(^{15}N_\beta{}^{13}C)$ *(Hz, ±0·5)*
1	7·40	121·2	3·5
2	—	143·4	8·8
3	—	128·5	3·0
4	—	176·2	
5	8·07	129·1	
6	6·95	116·6	
7	—	149·8	
8	7·01	113·7	
4a	—	122·4	
8a	—	137·6	
1′	—	143·0	6·7
2′	7·74	117·0	2·4
3′	7·47	129·6	
4′	7·23	125·5	

[a] δ(NH) = 16·20; δ(NH$_2$) = 6·40 (temperature- and concentration-dependent).

SpectroscopY (H,H-COSY),[16] heteronuclear shift-COrrelated SpectroscopY (H,C-COSY),[16] Nuclear Overhauser Effect SpectroscopY (NOESY)[16] and COrrelation via LOng range Couplings (COLOC)[17] techniques supplemented with one-dimensional selective INEPT[10] (Insensitive Nuclei Enhanced by Polarization Transfer).

Sodium salt of 7-amino-4-hydroxy-3-phenylazo-2-naphthalenesulfonic acid (I)

The ^1H and ^{13}C chemical shifts and the coupling constants $^nJ(^{15}N_\beta{}^{13}C)$ in the compound **I** at 300 K are given in Table 1. Figure 1 shows the H,H-COSY contour plot of the compound **I**, the ^1H-NMR spectrum being along both axes. The off-diagonal peaks (cross peaks) occur only if the spins at two appropriate frequencies are spin-coupled with $J(H(i)H(j))$ and these peaks have the coordinates $\delta(H(i))$; $\delta(H(j))$ and $\delta(H(j))$; $\delta(H(i))$. Hence, examination of the pattern of off-diagonal peaks reveals the coupling pattern of the protons in **I**. The one-dimensional high-field ^1H-NMR spectrum of **I**, especially after line narrowing, can be easily analysed, but the H,H-COSY contour plot reveals also weak couplings $^5J(H(1)H(5))$ and $^4J(H(1)H(8))$, the existence of which can be used for assignment purposes (see assignment for the compound **II**) and the H,H-COSY spectrum serves as a starting position for studying the NOESY spectrum. In the NOESY spectrum (Fig. 2) scalar

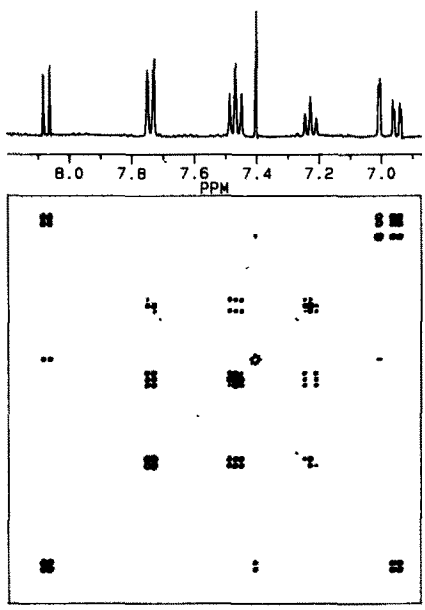


Fig. 1. Contour plot of homonuclear shift-correlated spectrum (H,H-COSY) of **I**.

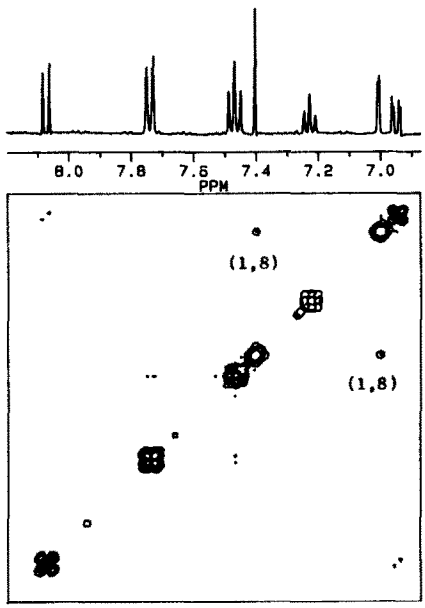


Fig. 2. Contour plot of NOESY spectrum of **I**.

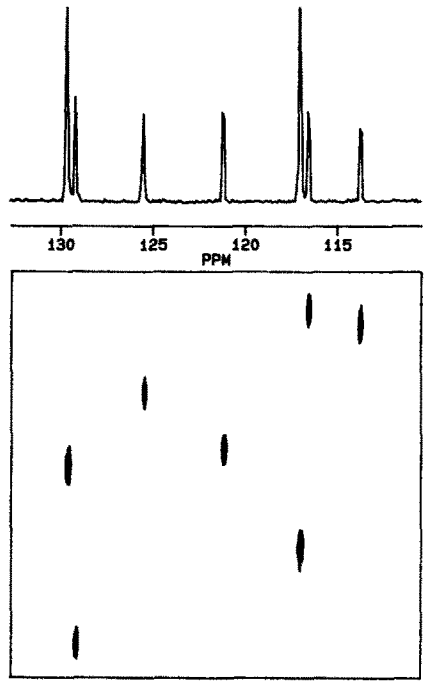


Fig. 3. Contour plot of heteronuclear shift-correlated spectrum (H,C-COSY) of **I**.

coupling correlations are strongly reduced by random variations of the mixing pulse.[16] Off-diagonal peaks (1, 8) correlate spins which share a dipolar coupling, i.e. protons H(1) and H(8) must be in the *peri* position. The NOESY spectrum is of the greatest importance for deciding the diazo coupling position of benzenediazonium chloride. Having assigned the ^{1}H-NMR spectrum we measured the heteronuclear shift-correlated spectrum (H,C-COSY) of **I**, shown in Fig. 3. Using only one experiment, connections between protons and CH carbons are established. The contour plot (Fig. 3) has ^{1}H shifts on the vertical axis (spectrum not shown) and ^{13}C shifts of CH

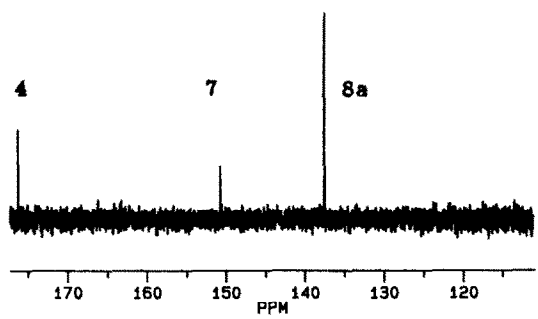


Fig. 4. Selective INEPT spectrum via ^3J(C(i)H(5)) of **I**.

carbons on the horizontal axis, with cross peaks indicating the correlations between the above-mentioned two types of nuclei. One-dimensional selective INEPT[10] is a method for selective polarization transfer via long-range CH couplings and this method was used for the assignment of quaternary carbons. As an example, Fig. 4 shows the selective INEPT spectrum via long-range $^3J(C(i)H(5))$. Selective ^{15}N-labelling ($N_\beta = 96{\cdot}2\%$ ^{15}N) makes it possible to measure absolute values of the coupling constants $^nJ(^{15}N_\beta{}^{13}C)$ and these values, showing known stereochemical dependence,[18] were also used for the assignment of some carbons.

Sodium salt of 5-amino-4-hydroxy-3-phenylazo-2,7-naphthalenedisulfonic acid (II)

The ^1H and ^{13}C chemical shifts and the coupling constants $^nJ(^{15}N_\beta{}^{13}C)$ in the compound **II** at 300 K are shown in Table 2. The ^1H-NMR spectrum (Fig. 5) reveals the existence of the coupling constant $^4J(H(6)H(8)) = 1{\cdot}3$ Hz and the H,H-COSY spectrum (Fig. 5) shows weak cross peaks due to $^4J(H(1)H(8))$ (compare with the compound **I**). Cross peaks (1,8) in the

TABLE 2

^1H and ^{13}C Chemical Shifts and Coupling Constants $^nJ(^{15}N_\beta{}^{13}C)$ of Compound **II** in Hexadeuteriodimethyl Sulfoxide at 300 K

H/C number	$\delta(^1H)^a$	$\delta(^{13}C)$	$^nJ(^{15}N_\beta{}^{13}C)$ *(Hz, ±0·5)*
1	7·32	122·8	3·5
2	—	142·7	8·8
3	—	129·0	3·7
4	—	181·5	
5	—	[b]	
6	7·08[c]	112·1	
7	—	[b]	
8	6·91[c]	113·5	
4a	—	112·3	
8a	—	136·5	
1′	—	142·8	6·7
2′	7·71	116·7	2·4
3′	7·44	129·6	
4′	7·17	124·9	

[a] $\delta(N\underline{H}) = 15{\cdot}49$; $\delta(N\underline{H}_2) = 7{\cdot}99$ (temperature- and concentration-dependent).
[b] 153·1 or 153·2.
[c] $^4J(HH) = 1{\cdot}3$ Hz.

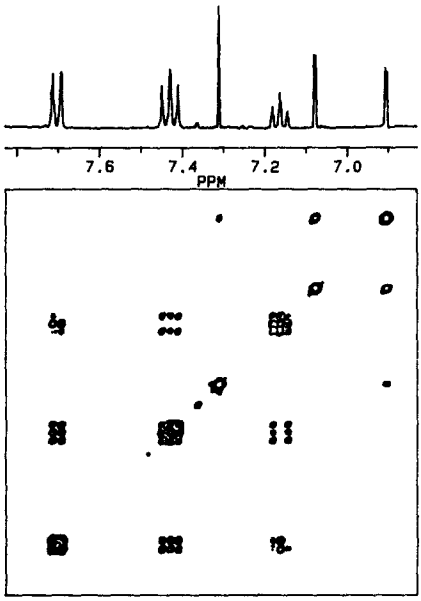


Fig. 5. Contour plot of homonuclear shift-correlated spectrum (H,H-COSY) of **II**.

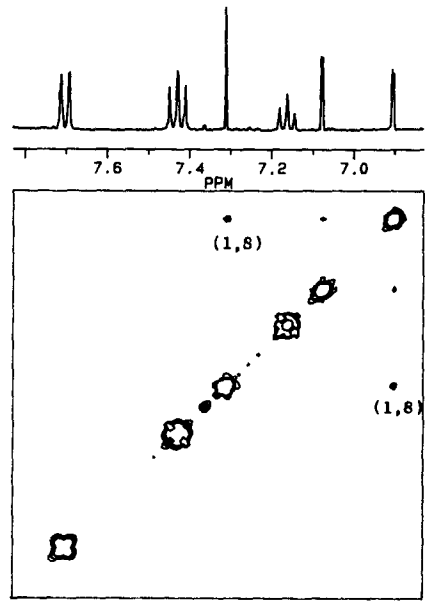


Fig. 6. Contour plot of NOESY spectrum of **II**.

NOESY spectrum (Fig. 6) indicate clearly the proximity of protons H(1) and H(8). The H,C-COSY, selective INEPT spectra and $^{n}J(^{15}N_{\beta}{}^{13}C)$ were used for assignment of carbon chemical shifts.

Sodium salt of 6-amino-4-hydroxy-3-phenylazo-2-naphthalenesulfonic acid (III)

The ^{1}H and ^{13}C chemical shifts and the coupling constants $^{n}J(^{15}N_{\beta}{}^{13}C)$ in the compound **III** at 300 K are reported in Table 3. Small differences of 0·01 and 0·02 ppm, respectively, in ^{1}H-NMR chemical shifts were found among δ(H(5)), δ(H(3′)) and δ(H(8)) in the ^{1}H-NMR spectrum after line narrowing. The assignment was based on the different coupling pattern of appropriate signals and on the results of the selective homonuclear decoupling. ^{13}C chemical shifts of CH groups were assigned using the H,C-COSY spectrum, whilst for assignment of signals of quaternary carbons COLOC[17] spectra were used.

^{15}N-NMR spectra

The temperature dependence of the ^{15}N chemical shifts, the coupling constants $^{1}J(^{15}NH)$ and the hydrazone-form contents of compounds **I**–**III** in hexadeuteriodimethyl sulfoxide are given in Table 4. Different values of the

TABLE 3

^{1}H and ^{13}C Chemical Shifts and Coupling Constants $^{n}J(^{15}N_{\beta}{}^{13}C)$ of Compound **III** in Hexadeuteriodimethyl Sulfoxide at 300 K

H/C number	$\delta(^{1}H)^{a}$	$\delta(^{13}C)$	$^{n}J(^{15}N_{\beta}{}^{13}C)$ *(Hz, ±0·5)*
1	7·52	122·4	3·9
2	—	137·7	8·3
3	—	129·4	2·9
4	—	176·2[b]	
5	7·49	109·6	
6	—	149·3	
7	7·07	121·4	
8	7·46	130·6	
4a	—	132·3	
8a	—	125·6	
1′	—	143·6	6·8
2′	7·82	118·0[c]	2·4
3′	7·48	130·0	
4′	7·26	126·5	

[a] $\delta(N\underline{H}) = 16{\cdot}14$; $\delta(N\underline{H}_2) = 5{\cdot}80$ (temperature- and concentration-dependent).
[b] 174·9 at 360 K.
[c] 117·7 at 360 K.

TABLE 4

Temperature Dependence of ^{15}N Chemical Shifts, Coupling Constants $^{1}J(^{15}NH)$ and Hydrazone-form Content of Compounds **I–III** in Hexadeuteriodimethyl Sulfoxide

Compound	*Temperature (K)*	$\delta(^{15}N_{\alpha})$	*Hydrazone form[a] (%)*	$\delta(^{15}N_{\beta})$	*Hydrazone form[a] (%)*	$^{1}J(^{15}NH)$ *(Hz)*	*Hydrazone form[a] (%)*
I	300	−184·4	92·4	4·6	84·8	91·8	95·6
	360	−180·4	90·7	7·7	83·3	88·4	92·1
II	300	−200·6	98·3	−7·6	93·3	94·3	98·2
	360	−199·3	97·5	−5·3	92·2	94·0	97·9
III	300	−174·7	88·9	10·2	80·9	86·0	89·6
	360	−163·4	84·6	17·9	76·3	81·2	84·6

[a] Calculated from the data in the preceding column (see text).

^{15}N enrichment enables us to assign the ^{15}N chemical shifts unambiguously.[19] Hydrazone-form contents obtained from the ^{15}N chemical shifts were calculated using the procedure described in ref. 11. Hydrazone-form contents obtained by means of $^1J(^{15}NH)$ were calculated using eqn (1):[13]

$$\text{Percentage of hydrazone form} = 100 \times {}^1J(^{15}NH)_{exp}/{}^1J(^{15}NH) \quad (1)$$

using $^1J(^{15}NH) = 96$ Hz.[13]

We have found that compounds **I–III** exist, in hexadeuteriodimethyl sulfoxide solutions, as equilibrium mixtures of the azo and hydrazone tautomers with strongly prevailing naphthoquinone phenylhydrazone configurations. Relatively small differences in hydrazone-form contents (Table 4), calculated from $\delta(N_\alpha)$, $\delta(N_\beta)$ and $^1J(^{15}N_\alpha H)$, follow from the choice of standards. ^{13}C chemical shifts of C(1′), C(2′) and C(4′)[20] and C(3)[21] also support strongly prevailing naphthoquinone phenylhydrazone configurations (Tables 1–3).

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