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An NMR Study on Molecular Interactions in 3-Methylsydnone and Its Aqueous Mixtures

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Molecular motion in neat 3-methylsydnone and molecular interaction in 3-methylsydnone–water mixtures were studied by the multinuclear FT-NMR method. The estimated rotational correlation times of the methine carbon and the carbonyl oxygen atom in neat sydnone are 8.6 and 8.1 ps at 40 °C, respectively. According to shift variations of the ^{13}C, ^{14}N, and ^{17}O nuclei of the sydnone molecule in sydnone–water mixtures, the sydnone forms a hydrogen bond with water at the carbonyl oxygen and not at the ring oxygen site. The effect of dissolved paramagnetic ions was investigated on the ^{13}C spin-lattice relaxation time of the carbon atoms of sydnone, and a discussion was made on the possible relative configuration of cation and anion to the solvent sydnone molecule.

The group of sydnones is a prototype for the general class of mesoionic compounds which cannot satisfactory be represented by Lewis forms involving no charge separation. The structure and reactions of sydnones were studied extensively.[1–3] Recently Lemire and Sears[4] measured bulk physical properties of 3-methylsydnone (Fig. 1), pointing out that it would be a promising nonaqueous solvent; its dipole moment is 7.3 D (1 D=3.3356×10^{-30} cm) and its relative permittivity for the liquid phase is 144.0 (40 °C). In their subsequent work,[5] interaction of 3-methylsydnone with water and solvation of ions dissolved in the sydnone were studied by determining bulk properties of sydnone–water mixtures and conductivities of ions in the sydnone, respectively. In the present study, we examined four aspects of solvent properties of 3-methylsydnone by the multinuclear FT-NMR method: First, to investigate the self-association of the sydnone, we measured the ^{13}C spin-lattice relaxation time of the methine carbon C(4) and the ^{17}O spin-spin relaxation time of the carbonyl oxygen O(6), and discussed on the molecular motion in neat 3-methylsydnone. Second, to investigate the electron accepting ability of the sydnone, pyridine was used as a probe; we measured the ^{13}C spin-lattice relaxation time of the pyridine carbon atoms in an equimolecular mixture with the sydnone to detect any association of pyridine with the sydnone at the pyridine nitrogen atom. Third, to identify proton-accepting sites in 3-methylsydnone, measurements were made of chemical shift variations of the ^{1}H, ^{13}C, ^{14}N, and ^{17}O nuclei of the sydnone with dilution of the sydnone with D_2O. On the basis of these data we attempted to determine the site at which the sydnone is hydrogen-bonded to water. Fourth, to investigate solvation of ions in 3-methylsydnone paramagnetic ions were used; we measured the ^{13}C spin-lattice relaxation time of the sydnone carbon atoms before and after addition of a paramagnetic cation or anion, and then attempted to determine the relative configuration of the ion to the sydnone molecule.

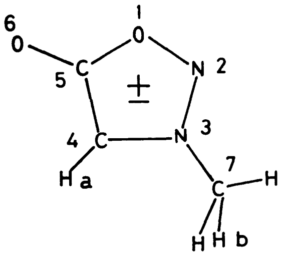

Fig. 1. Structure and numbering of the atoms of 3-methy lsydnone.[5]

Experimental

3-Methylsydnone was synthesized from *N*-methylglycine by the method of Vasil'eva and Yashunskii,[6] and purified by the zone melting method. The final freezing point of the purified sydnone was 36 °C. Pyridine, paramagnetic reagents, and deuterium oxide were commercially available and used without further purification. 3-Methylsydnone–D_2O and –pyridine mixtures were prepared on the weight basis. NMR sample tubes for relaxation time measurement were degassed on a vacuum line by at least three freeze-pump-thaw cycles and sealed before use. All NMR experiments were performed on naturally abundant materials.

NMR measurements were carried out on a JEOL FX-90Q spectrometer operating in the Fourier transform mode. A JEOL Temperature-controller (NM-VTS) with a thermocouple external to the sample was used to monitor the probe temperature within 1 K. The ^{13}C spin-lattice relaxation time was obtained from satandard inversion-recovery FT-NMR experiments. The ^{14}N spectrometer frequency was 6.42 MHz and 8192 data points were used for a 4 kHz spectral width. Pulses with 8 μs width and 1.0 s interval were used for each scan. Averaging 1000 scans were sufficient to get a reasonable S/N ratio for the signal of the N(3) atom of sydnone. The experimental error for the reported ^{14}N chemical shifts is within ±0.1 ppm. The ^{17}O spectral parameters were as follows: spectrometer frequency, 12.10 MHz; spectral width, 10 kHz; pulse interval, 40 ms; pulse width, 10 μs: 512 data points were used. Normally, 10^6 scans were adequate for obtaining a well resolved ^{17}O NMR signal. The ^{17}O spin-spin relaxation time was calculated from $T_2=(\pi\Delta\nu_{1/2})^{-1}$, where $\Delta\nu_{1/2}$ is the full width at the half height of absorption signal in Hz. The accuracies for the reported T_2 and chemical shifts were estimated as ±10% and ±10 ppm, respectively. The temperature was 40±1 °C except for the shift measurement for the O(1) atom in 3-methylsydnone. Since the absorption signal of O(1) was too broad at 40 °C, we could obtain no precise shift values. The shift variation was measured at 100 °C.

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Table 1. Chemical shifts of atoms in neat 3-methylsydnone

Atom	Chemical shift/ppm	Reference[a]
O(1)	389	External D_2O
N(2)	Very broad	—
N(3)	252.1	External NH_4^+ (NH_4NO_3)
C(4)	97.66	External TMS
C(5)	170.66	External TMS
O(6)	234	External D_2O
C(7)	40.43	External TMS
H(a)	6.895	Internal DSS
H(b)	4.307	Internal DSS

a) The relative shift based on the external referencing was corrected for the difference in bulk susceptibility between the sample and the reference compound.

Results and Discussion

Assignment of NMR Signals. Table 1 presents the chemical shifts of the ^{1}H, ^{13}C, ^{14}N, and ^{17}O atoms of neat 3-methylsydnone. The assignment of the NMR signals, except for the ^{17}O atoms, is based on shift data reported in the literature.[7–11] The assignment of the two ^{17}O NMR signals is based on the assumption that the NMR signal of the ^{17}O atom with higher local electron density appears at higher field.[12] Eckert-Maksić and Maksić[13] estimated the local electron density of the atoms in 3-methylsydnone by means of MO calculation (MNDO). We utilized their results on the assignment of the ^{17}O signals.

Molecular Motion and Self-association in Neat 3-Methylsydnone. Table 2 presents the ^{13}C spin-lattice relaxation time of the methine carbon C(4) and the ^{17}O spin-spin relaxation time of the carbonyl oxygen O(6) together with the estimated values for the rotational correlation time τ_c. The estimation of τ_c's is based on the assumption that the ^{13}C atom relaxes primarily through dipolar interaction with the directly bonded proton, whereas the ^{17}O atom does through quadrupole interaction with the filed gradient tensor of the molecule. The dipolar relaxation expression is given by

$$\frac{1}{T_1^{\mathrm{DD}}} = \frac{n_{\mathrm{H}}\gamma_{\mathrm{C}}\gamma_{\mathrm{H}}\hbar^2}{r_{\mathrm{C-H}}^6}\tau_c, \tag{1}$$

where n_H is the number of protons directly attached to the carbon of interest. The quadrupole relaxation expression is given by the following equation within the limits of extreme narrowing condition:[14]

$$\frac{1}{T_1^{\mathrm{Q}}} = \frac{1}{T_2^{\mathrm{Q}}} = \frac{3(2I+3)}{40\,I^2(2I-1)}\left(1+\frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{\hbar}\right)^2\tau_c, \tag{2}$$

where I is the spin quantum number, η is the asymmetric parameter, and e^2qQ/h is the quadrupole coupling constant (NQCC). The calculation of τ_c for the ^{13}C atom requires the value of carbon-hydrogen bond distance. We employed a C–H distance of 1.09 Å which is reasonable for the sp^2 carbon. The calculation of τ_c for the ^{17}O atom requires the value of NQCC and asymmetry parameter. There have been reported only a few ^{17}O NQR studies, and therefore we employed a NQCC of 10.2 MHz, which is the value for urea, and an asymmetric parameter $\eta=0.45$, which is the nominal value for the carbonyl oxygen.[15] Since the NQCC is included squared in the relaxation equation, the molecular correlation time as calculated from nuclear quadrupolar relaxation data is dependent highly on the NQCC value. The coupling constant for urea is in good agreement with the 10.6—10.9 MHz range of constants obtained for substituted benzaldehydes.[16]

Table 2. ^{13}C spin-lattice and ^{17}O spin-spin relaxation times and rotational correlation times of C(4) and O(6) atoms of 3-methylsydnone at 40 °C

Atom	T_1, T_2	τ_c /ps
$^{13}C(4)$	5.4 s	8.6
$^{17}O(6)$	1.1_8 ms	8.1

The estimated rotational correlation times for the methine carbon C(4) and carbonyl oxygen O(6) are nearly equal to each other. Since 3-methylsydnone is not a spherical top, it is possible that there will be a preferred axis of molecular rotation. Both Eqs. 1 and 2 essentially correspond to the isotropic molecular reorientation. The carbon $\tau_c(^{13}C)$, however, reflects the motions effective for reorienting each C–H vector, and the oxygen τ_c (^{17}O) reflects the motion most effective for reorienting the electric field gradients at the ^{17}O atom. Therefore, it can be inferred that the estimated correlation time for the methine carbon $\tau_c(^{13}C)$ corresponds to that for the reorientation of the C(4)–H vector and that the correlation time for the carbonyl oxygen $\tau_c(^{17}O)$ corresponds to that for the reorientation of the C(5)–O(6) vector. These two vectors are not parallel to each other. Thus the agreement between $\tau_c(^{13}C)$ and $\tau_c(^{17}O)$ leads us to a conclusion that the molecular reorientation of 3-methylsydnone is fairly isotropic.

If chain-like association as found in some amide systems[17] takes place in neat sydnone, the reorientation of aggregates is expected to be highly anisotropic. Thus, from the above discussion it may be concluded that such "anisotropic" association does not take place in neat 3-methylsydnone. We have estimated the radius of the molecule from the average correlation time for C(4) and O(6) by the Debye relation

$$\tau_c = \frac{4\pi r^3\eta}{3kT}, \tag{3}$$

where r is the molecular radius, η is the macroscopic shear viscosity, k is the Boltzmann constant, and T is the absolute temperature. The estimated molecular radius is 1.2 Å. This result suggests that 3-methylsydnone does not form large aggregates. The intermolecular interactions in neat 3-methylsydnone seem weak and nonspecific. It is important, however, that the above discussion do not disprove the formation of aggregates which are small and rotating isotropically.

The Electron-accepting Ability of 3-Methylsydnone. Campbell *et al.*[18] proposed that pyridine is a useful probe for studying association of molecules when the interaction is weak and the life time of the complex is short. Pyridine has a basic lone electron pair at its nitrogen. The reorientation of pyridine, when the lone pair is free, is effectively isotropic and thus pyridine has nearly equal ^{13}C spin-lattice relaxation times for C(2), C(3), and C(4). When pyridine associates with a molecule on the lone pair site, the reorientation of the molecule becomes anisotropic. The formation of such complexes slows down the tumbling about the axis perpendicular to the C(4)–N(1) axis, and a change in rotational diffusion tensor can be detected by measuring the spin-lattice relaxation times for C(2), C(3), and C(4). They introduced a parameter R, defined as the ratio of the mean of the relaxation times of C(2) and C(3) to that of C(4), *i.e.*

$$R = \frac{T_1(\mathrm{C2}) + T_1(\mathrm{C3})}{2T_1(\mathrm{C4})}. \tag{4}$$

Table 3 presents the relaxation times of C(2), C(3), and C(4) of pyridine in the neat liquid and in an equimolar mixture with 3-methylsydnone, together with the estimated values of R. The addition of 3-methylsydnone does not change the R value. This result indicates that any charge-transfer complexes between pyridine and the sydnone do not form, and that 3-methylsydnone has no site on which the sydnone interacts with a basic lone pair.

Identification of the Proton-aceepting Site in 3-Methylsydnone. Chemical shifts of all the atoms except N(2) in 3-methylsydnone were measured in sydnone–D_2O mixtures at 40 °C. Figures 2 and 3 present chemical shift differences relative to the neat sydnone as a function of mole fraction of D_2O. 3-Methylsydnone has four lone-pair sites where the sydnone can be expected to form hydrogen bonds to water. As shown in Fig. 2, when 3-methylsydnone is diluted with D_2O, the carbonyl oxygen O(6) show a very large up-field shift, up to about 34 ppm at infinite dilution. It has been reported that the hydrated carbonyl oxygens of acetone, *N*-substituted formamides, and *N*-substituted acetamides show a large up-fieled shift (20—50 ppm).[12,19] As a significant aspect the experimental results show that the shift variation of the other atoms C(5), C(4), N(3), and C(7) decreases in this order; this indicates that an electron transfer from the ring to carbonyl oxygen takes place. These results lead us to the conclusion that 3-methylsydnone forms a hydrogen bond with water at the carbonyl oxygen site. The chemical shift of the ring oxygen O(1) is almost unchanged. Though the shifts were measured at 100 °C, we may conclude that no hydrogen bond is formed on this site of the sydnone. The NMR signal of the N(2) atom is too broad to be observed. We can, however, rule out the possibility that hydrogen bond will be formed only on this site: First, on the basis of MO calculation results,[13] protonation at the N(2) atom decreases the local electron density at the O(6) atom and thus if a hydrogen bond is to be formed at the N(2) atom, the carbonyl oxygen O(6) should show a down-field shift. This is against the experimental results. Second, formation of hydrogen bond at the N(2) atom will change electronic states of the atom adjacent to N(2) most effectively. Nevertheless, the shift variations of the O(1) and N(3) atoms are smaller than those of the other atoms of the ring. The above discussions are based on the assumption that the chemical shifts of ^{13}C, ^{14}N, and ^{17}O atoms are dependent predominantly on the paramagnetic nuclear screening

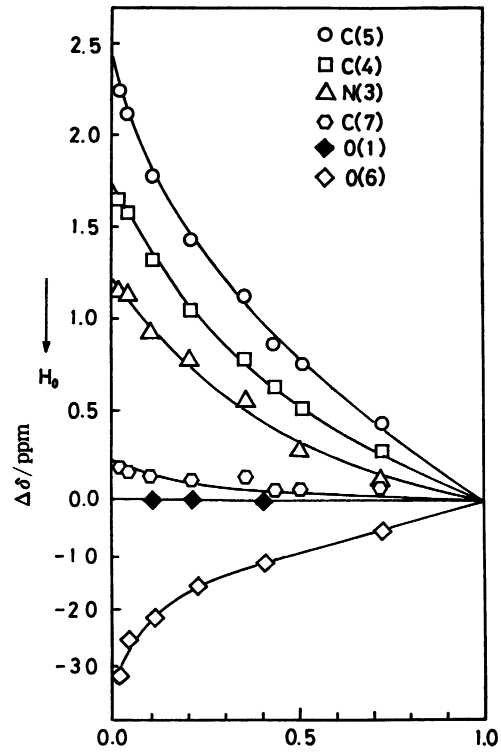

Fig. 2. The shift variations of ^{13}C, ^{14}N, and ^{17}O atoms in 3-methylsydnone–D_2O system.

TABLE 3. ^{13}C SPIN-LATTICE RELAXATION TIMES OF PYRIDINE

	T_1/s			R
	C(2)	C(3)	C(4)	
Neat pyridine	14.8	14.3	15.3	0.95
Pyridine–Sydnone mixture	12.0	12.6	13.0	0.94

TABLE 4. ^{13}C SPIN-LATTICE RELAXATION TIMES IN Mn^{2+}–SYDNONE AND $Cr(C_2O_4)_3{}^{3-}$–SYDNONE SYSTEMS

Ion	Atom	$T_{1\,\mathrm{dia}}$/s	$T_{1\,\mathrm{ob}}$/s	$T_1{}^{\mathrm{e}}$/s
Mn^{2+}	C(7)	5.3	2.3	4.1
	C(4)	5.4	0.98	1.2
	C(5)	50.5	0.25	0.25
$Cr(C_2O_4)_3{}^{3-}$	C(7)	5.3	0.37	0.40
	C(4)	5.4	0.43	0.47
	C(5)	50.5	0.83	0.84

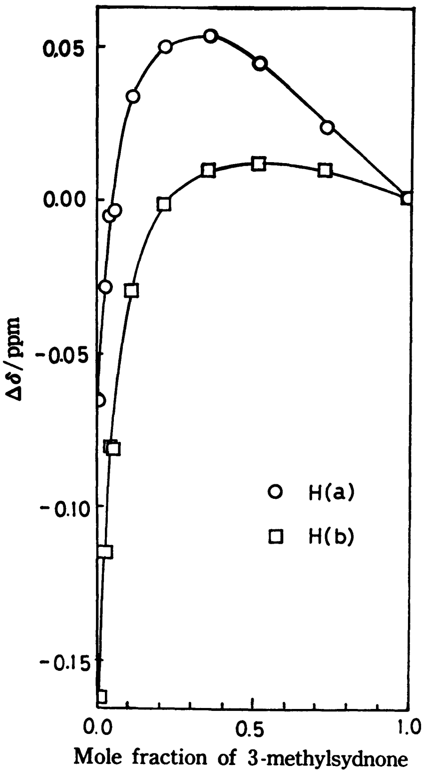

Fig. 3. The shift variations of the ^{1}H atoms of 3-methylsydnone in the sydnone–D_2O system.

constant σ_P so that the changes in chemical shift are due primarily to alternation in the local electron density at the atom.[12]

As shown in Fig. 3, as 3-methylsydnone is diluted with D_2O, the protons of the sydnone show a down-field shift at low dilution and an up-field shift at high dilution. The down-field shift variation can be explained in terms of the hydrogen bonding effect. The hydrogen bonds between the sydnone and water decrease the electron density of the sydnone ring so as to give rise to down-field shift of the proton. To interpret the up-field shift change, we assume that part of the sydnone molecules associate to form aggregates, whose protons are capable of resonance at lower fields than those of the monomer, possibly by the ring current effect. Thus, in sufficiently diluted solution, aggregates break out until the up-field shift effect has outweighed the hydrogen bonding effect.

The Solvation of Ions in 3-Methylsydnone. Table 4 presents the spin-lattice relaxation rates $1/T_1$ of the ^{13}C atoms in 3-methyl sydnone before and after addition of paramagnetic ions. From these results the relative configuration of ions to the sydnone molecule is to be considered. Paramagnetic relaxation reagents can interact with organic compounds to form collision type or electron-transfer type complexes and to change T_1's of the atoms in the molecule according to the electron-nuclear dipole-dipole relaxation mechanism. This relaxation mechanism has a reciprocal sixth-power distance dependence and no angle dependence. Atoms close to the site of complexation will have shortest T_1 values. We have estimated the electron-nuclear d-d relaxation time of the atoms in the molecule. The effect of a paramagnetic reagent on T_1 is given by

$$\frac{1}{T_{1\,\mathrm{ob}}} = \frac{1}{T_{1\,\mathrm{dia}}} + \frac{1}{T_1{}^{\mathrm{e}}}, \tag{5}$$

where $1/T_{1\,\mathrm{op}}$ is the observed relaxation rate, $1/T_{1\,\mathrm{dia}}$ is the sum of all diamagnetic relaxation rates, and $1/T_1{}^{\mathrm{e}}$ is the relaxation rate according to the electron-spin d-d relaxation mechanism. Levy and Komoroski[20] pointed out that the atoms in a given molecule may be under a considerable effect from relaxation reagent ions that are not complexed, being led to formulate

$$\frac{1}{T_1{}^{\mathrm{e}}} = \frac{X_{\mathrm{f}}}{T_{1\mathrm{f}}{}^{\mathrm{e}}} + \frac{X_{\mathrm{c}}}{T_{1\mathrm{c}}{}^{\mathrm{e}}}, \tag{6}$$

where $1/T_1{}^{\mathrm{e}}$ is the total relaxation rate for the electron-nuclear dipolar interaction, $1/T_{1\mathrm{f}}{}^{\mathrm{e}}$ and $1/T_{1\mathrm{c}}{}^{\mathrm{e}}$ are the rates when the molecule is free and complexed, respectively, and X_{f} and X_{c} are the respective molar fractions. Since X_{f}, X_{c}, and $T_{1\mathrm{f}}{}^{\mathrm{e}}$ are common for given atoms in a molecule, $T_{1\mathrm{c}}$ may be taken to be proportional to the reciprocal sixth power of distance R from the atom of interest to the relaxation reagent. Thus we have

$$\frac{1}{T_1{}^{\mathrm{e}}} = \alpha\frac{1}{R^6} + \beta, \tag{7}$$

where α and β are positive constants. By positioning systematically the paramagnetic ion relative to the 3-methylsydnone molecule, we have calculated the distances from the carbon atoms to the ion. The bond lengths and angles for the sydnone used in the calculation are based on the X-ray analysis on 4,4'-dichloro-3,3'-ethylenebissydnone by Thiessen and Hope.[21] From these distances and the experimental relaxation rates, parameters α and β were calculated by the least-square procedure, and then the variances was estimated by

$$\text{Variance} = \log\left(\sum\left\{\frac{1}{T_{1\,\mathrm{ob}}{}^{\mathrm{e}}} - \frac{1}{T_{1\,\mathrm{cal}}{}^{\mathrm{e}}}\right\}\right), \tag{8}$$

where $1/T_{1\,\mathrm{ob}}{}^{\mathrm{e}}$ and $1/T_{1\,\mathrm{cal}}{}^{\mathrm{e}}$ are the observed and calculated relaxation rates, respectively. If the variance is less than -4 and both α and β are positive for a given position, the ion can be taken to exist at the position.

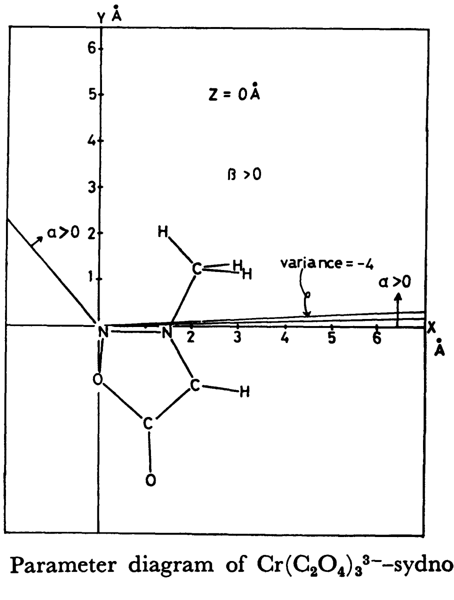

Fig. 4. Parameter diagram of $Cr(C_2O_4)_3{}^{3-}$–sydnone system.

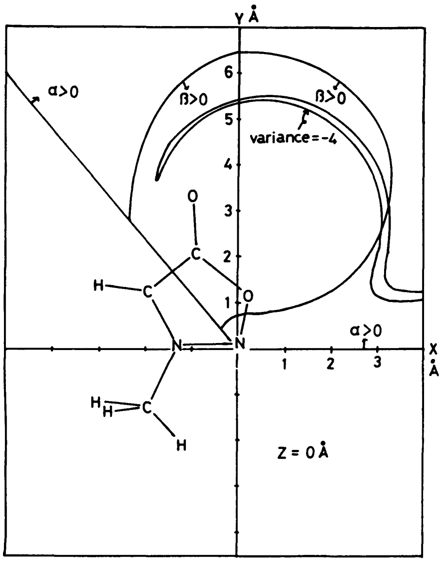

Fig. 5. Parameters diagram of Mn^{2+}–sydnone system.

This threshold value of −4 has been determined from the experimental error for the T_1 measurement of ±5%. Figures 4 and 5 illustrate contour diagrams of the variance for anion and cation, respectively. Since we have not a fitting point but a fitting surface as shown in these figures, we cannot quantitatively specify the relative positions of the ions. We can, however, obtain information on the site of ion solvation in 3-methylsydnone from these results. The methine proton and methyl group with large positive formal charge¹³⁾ are closest to the anion. For the cation, on the other hand, the carbonyl oxygen and ring oxygen with large negative formal charge and lone pairs of electron are closest to the ion. The NMR signal of the carbonyl carbon is broadened by addition of Mn^{2+} ion. The broadening can be explained in terms of contact interaction of the unpaired electron of the ion with the carbon.

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