

A STUDY OF THE STRUCTURE OF SODIUM MONOHYDRO-TRIS(2-METHOXYETHOXO)BORATE*

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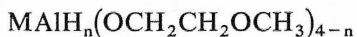
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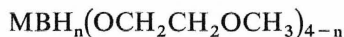
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The structure of sodium monohydro-tris(2-methoxyethoxo)borate was proposed on the basis of determination of the molecular weight and study of the ¹H- and ¹¹B-NMR and IR spectra. The hydride is a dimer in the entire measured concentration range and is in equilibrium with sodium tetrakis(2-methoxyethoxo)borate. The similarity of the structure to the aluminium analogue, sodium monohydridotris(2-methoxyethoxo)aluminate is discussed.

The structure of sodium monohydrido-tris(2-methoxyethoxo)aluminate (*Ib-2*) was recently proposed in our laboratories on the basis of the IR study of sodium and lithium¹ hydridoalkoxoaluminates; this substance is practically a dimer over a broad concentration range and behaves as an individual chemical species in solution². Sodium monohydro-tris(2-methoxyethoxo)borate (*Iib-2*) has recently been prepared in connection with research on the properties and reactivity of sodium hydridoalkoxoaluminates with a second donor atom in the β-position of the alkoxy; similar to *Ib-2*, this substance is practically infinitely soluble in ethers and aromatic hydrocarbons and is somewhat more than a dimer in the measured concentration region³. Hydrides *Ib-2* and *Iib-2* are somewhat stronger reducing agents than the corresponding complex trialkoxyhydrides with simple alkoxy (e.g. NaYH(OCH₃)₃, where Y = B or Al) (ref.^{4,5}). If we consider the fact that the ¹H-NMR spectra and the valence



I



II

a M = Li, *b* M = Na, *c* M = K, *d* M = (CH₃CH₂)₄N

I n = 0, 2 n = 1, 3 n = 2, 4 n = 4.

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vibration region of the C—O—C bonds of the β -methoxyethoxyl in the IR spectra of both hydrides are similar, then the possibility that *Ib-2* and *Iib-2* have similar structures in solution can be considered. A simple analogy is, however, excluded by the fact that the boron atom in hydridoalkoxoborates cannot attain a coordination number greater than 4, while the proposed structure of hydride *Ib-2* assumes that an aluminium atom has a coordination number of 6 to a slight degree². These facts formed a basis for a deeper study of hydridoalkoxoborate *Iib-2*.

The ¹¹B-NMR spectrum of a 15% benzene solution of a substance whose analysis corresponds to the formal formula *Iib-2* exhibits a doublet at $\delta = -6.6$ ppm (vs $\text{BF}_3(\text{CH}_2\text{CH}_3)_2\text{O}$), $J = 115$ Hz and a singlet at $\delta = -2.0$ ppm (according to reference³ for a 30% benzene solution, $\delta = -5.4$ ppm, $J = 125$ Hz and also $\delta = -1.7$ ppm), corresponding to monohydridotrialkoxoborate *Iib-2* and tetraalkoxoborate *Iib-1* in a ratio of 4 : 1. Analysis indicates that the solution also contains 4 mol% NaBH_4 in equilibrium composition. The degree of association of hydrides *Iib-2* in benzene equals 2.3 and does not change over the concentration range 2–15%. With sodium tetrakis(2-methoxyethoxy)borate *Iib-1* and for the benzene soluble complex of *Iib-1* with sodium tetrahydridoborate *Iib-4* corresponding formally to $\text{NaBH}_{1.67}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{2.33}$ (*III*) (ref.⁶), the molecular weight increases with increasing concentration and the degree of association is always greater than 20. Consequently, it can be assumed that *Iib-2* exists in solution primarily as a dimer.

The ¹H-NMR spectra of complexes *Iib-2* (Fig. 1) and the spectra of the other measured benzene solutions of *I* and *II* generally contain simple triplets corresponding to the α and β -methylene groups of the alkoxy and a singlet corresponding to the β -methoxyl (Table I). No further peaks appear in the toluene solutions at low tempera-

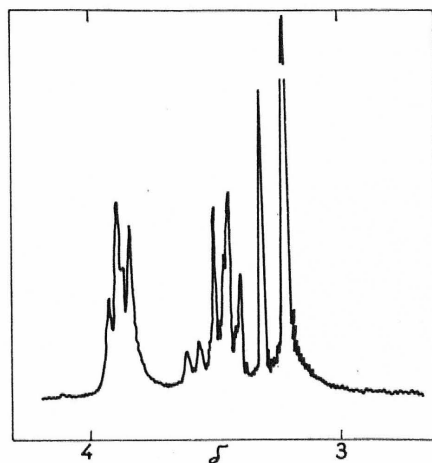


FIG. 1

The ¹H-NMR Spectrum of a 15% Solution of Sodium Monohydro-tris(2-methoxy-ethoxy)borate (*Iib-2*)

tures; if the temperature of solutions of complex *I* or *II* falls to -100°C , the signals broaden and the triplets merge to give broad singlets. In alkoxyhydrides and aluminium alkoxides of type *IV*, where at least some alkoxy groups form a rigid skeleton, the α and β -methylene groups of the rigid alkoxy produce a broad symmetrical multiplet and the free alkoxy yields a simple triplet⁷. In substances *I* and *II*, the presence of a completely free alkoxy group, not solvating the alkaline metal or aluminium atom, is improbable. Apparently the equilibrium among the individual coordination bonds is too fast to be observed by NMR.



IV

In the alkoxy signal region the spectra of compounds *I* and *II* are very similar. Hydride *Id-3* with a tetraethylammonium cation is an exception; here the α and β -methylene hydrogens appear as a multiplet. The proton spectrum of substance *Iib-2* is also different (Fig. 1) as, in addition to the α -methylene ($\delta = 3.88$ ppm, $J = 5$ Hz) and β -methylene ($\delta = 3.45$ ppm, $J = 5$ Hz) triplets and a methoxyl singlet ($\delta = 3.21$ ppm), a further, partially obscured triplet is present to a greater degree in the β -methylene region ($\delta = 3.56$ ppm, $J = 5$ Hz), along with a further singlet in the methylene hydrogen region ($\delta = 3.30$ ppm). It follows from the ratio of the intensities of the methoxyl hydrogen signals and from the ^{11}B -NMR spectrum that the substances are present in a ratio of 4 : 1. It follows from these results and comparison of the ^1H -NMR spectra of substances *Iib-2* and *Iib-1* (Table I) that the second less intense β -methylene triplet and the second singlet can be assigned to the 2-methoxyethoxyl complex of *Iib-1* with *Iib-4*.

The described spectra of compounds *I* and *II* and the spectra of benzene solutions of mixtures of *I-1* + *I-2* and *II-1* + *II-4* (ref.⁸) indicate that *Iib-2* exists in solution in the presence of the corresponding tetralkoxoborate *Iib-1* in equilibrium with slow exchange at temperatures up to $+70^{\circ}\text{C}$. In compounds *Iia* and *Iic*, the alkoxy and the hydride hydrogen cannot be bound to the same boron atom⁶ and in the aluminium analogues of *I* the exchange between the individual hydridoalkoxoaluminates is very rapid on the NMR time scale, even at -100°C .

In compound *Ib-2* an equilibrium is considered² to exist between two structures where aluminium has coordination number 5 and to a small degree 6 and where all the oxygen atoms of the alkoxy groups are also coordinated to either aluminium or sodium atoms. Structure *V* with pentacoordinated aluminium is present in much larger amounts. In the boron analogue *Iib-2* further coordination of the four coordinated boron is not possible and thus the only position considered for solvation of the oxygen atoms is on the sodium atom. The *Iib-2* molecule contains three 2-methoxyethoxy groups so that 6 oxygen atoms could take part in solvation of one sodium

atom. It is generally assumed that the sodium cation can be solvated by up to four ether, amine or water molecules⁹⁻¹¹, although the coordination number of sodium in the presence of polyethers $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$ can be as large as 5 (ref.¹²),

TABLE I

The ¹H-NMR Spectra of Hydridoalkoxoaluminates (I) and Hydroalkoxoborates (II) in 5% Benzene Solutions at 37°C (chemical shift in δ , coupling constants in Hz)

Compound	$\alpha\text{-CH}_2^a$	$\beta\text{-CH}_2^a$	CH_3O^a	Other
<i>Ia-1</i>	4.03 (t; $J = 5$)	3.44 (t; $J = 5.5$)	3.26 (s)	
<i>Ia-2</i>	4.02 (t; $J = 5$) ^b	3.44 (t; $J = 5.5$) ^b	3.25 (s)	
<i>Ia-3</i>	3.80 (t; $J = 4.5$)	3.12 (t; $J = 5$)	3.07 (s)	
<i>Ib-1</i>	4.03 (t; $J = 4.5$)	3.48 (t; $J = 4.5$)	3.25 (s)	
<i>Ib-2</i>	3.96 (t; $J = 4.8$)	3.41 (t; $J = 5$)	3.24 (s)	
<i>Ib-3</i>	3.91 (t; $J = 5$)	3.38 (t; $J = 5$)	3.25 (s)	
<i>Id-1</i> ^c	4.23 (t; $J = 5.5$)	3.68 (t; $J = 5.5$)	3.34 (s)	
<i>Id-2</i> ^c	4.24 (t; $J = 6$) ^d	3.69 (t; $J = 5.5$) ^d	3.34 (s)	
<i>Id-3</i> ^{c,e}	4.14-4.36 (m)	3.60-3.74 (m)	3.35 (s)	
<i>Ila-1</i>	3.94 (s) ^f	3.68 (s) ^f	3.35 (s)	
<i>Ila-2</i> ^g	3.78 (t; $J = 4.5$)	3.46 (t; $J = 5$)	3.25 (s)	
			3.22 (s) ^h	
<i>Ila-3</i> ⁱ	3.79 (t; $J = 4.5$)	3.43 (t; $J = 5$)	3.26 (s)	0.15 (q; $J = 80$) ^j
			3.19 (s) ^h	
<i>Ilb-1</i>	3.86 (t; $J = 5$)	3.61 (t; $J = 5$)	3.36 (s)	
<i>Ilb-2</i>	3.88 (t; $J = 5$)	3.45 (t; $J = 5$)	3.21 (s)	
		3.56 (t; $J = 5$)	3.30 (s) ^k	
<i>III</i> ^l	3.91 (t; $J = 5$)	3.46 (t; $J = 5$)	3.28 (s)	
		3.58 (t; $J = 5$)	3.33 (s) ^h	
<i>Ilc-1</i>	3.78 (t; $J = 5$)	3.53 (t; $J = 4.5$)	3.33 (s)	
			3.19 (s) ^h	

^a s Singlet, t triplet, q quadruplet. Chemical shift in ppm (δ scale) relative to tetramethylsilane. The signals of the compounds in each region are ordered with decreasing integral intensity.

^b Triplet (multiplet) is poorly resolved. ^c Signals corresponding to the tetraethylammonium cation are not given in the table. ^d Triplet overlapping with a weaker multiplet. ^e In benzene solution only a substance corresponding to the formal formula $(\text{CH}_3\text{CH}_2)_4\text{NAIH}_{1.5}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{2.5}$ could be prepared. ^f Broad signal, apparently an unresolved triplet. ^g The substance corresponding to the formal structure *Ila-2* contains only $\text{B}(\text{OR})_3$ and BH_4 groups according to the ¹¹B-NMR spectra (ref.⁶). ^h According to an integral intensity less than 8% of the stronger methoxy group signal. ⁱ The substance corresponding to formal structure *Ila-3* is $\text{LiBH}_4 \cdot \text{LiB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4$ (ref.⁶); the concentration of the benzene solution is 40%. ^j Signal of the hydrogens of the BH_4 group. A broad quadruplet. ^k Integral intensity 20% of the stronger methoxy group signal. ^l In benzene solution, only a compound corresponding to the formal formula $\text{NaBH}_{1.67}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_{2.33}$ could be prepared instead of *Ilb-3* (ref.⁶).

in dimethyl sulphoxide 6 (ref.¹³) and is considerably larger in macrocyclic "crown" polyethers^{14,15}. The latter do not, of course, involve classical donor-acceptor solvation; cyclic polyethers are the strongest known solvation agents, in spite of the fact that they are planar¹².

If the electron pair of the ether oxygen participates in the solvation, the electron density around the protons bound to the neighbouring carbon atoms decreases and its ¹H-NMR signal shifts to lower field strengths^{9,15}. In the presence of aromatic anions (fluorenyl), solvation of cations of alkali metals leads, on the other hand, to a shift of the proton signals of solvated ethers to higher fields¹⁶⁻¹⁸. The authors explained this phenomenon by the shielding effect of the aromatic anion ring in the neighbourhood of the solvated cation and consequently also of the ether molecule. This anomalous shift is much larger if the solvating agent is a linear polyether^{16,17} or a cyclic "crown" ether¹⁸. In the solvation of lithium in LiAl(CH₃)₄ by 1,2-dimethoxyethane, the signals of all the ether protons are shifted upfield in benzene solutions and downfield in dichloromethane¹⁹. The authors explain this observation by formation of the LiAl(CH₃)₄-1,2-dimethoxyethane-benzene complex, where the C₆ axis of the benzene nucleus passes through the lithium atom. Then the methylene and methoxy protons lie in the area shielded by the aromatic ring; it is, however, generally true that protons in the neighbourhood of the axis of an aromatic nucleus are shielded, while the remaining protons close to the ring plane are less shielded^{19,20}.

A shift to higher fields was also observed in the spectra of some cryptates solvating the cations of alkali metals which they completely surround and enclose²¹⁻²³. It is possible that the cryptate signal lies at higher field strengths when the alkali metal cation is sufficiently large to fill the space within the ligand^{24,25}. In solvation of smaller cations there is a tendency for the cavity to contract, resulting in interligand repulsion which produces a less stable complex²⁴⁻²⁶.

In verification of the effect of benzene as a solvent the ¹H-NMR spectrum of *Iib-2* was measured in dichloromethane (a singlet corresponding to the methoxy group at $\delta = 3.36$ ppm and a multiplet at $\delta = 3.42-3.62$ ppm corresponding to the α and β methylene groups) and in dioxane (a singlet at $\delta = 3.35$ and methylene signals concealed under solvent signals in the $\delta = 3.45-3.70$ ppm region). As the spectra of other compounds *II* change in a similar manner (*e.g.* *Iia-3* in dichloromethane has a singlet at $\delta = 3.38$ ppm and a multiplet at $\delta = 3.44-3.60$ ppm), it appears that the benzene molecule is located in a certain manner in the neighbourhood of molecule *II*. Analogous solvation of *Ib-3* was demonstrated by Duben and co-workers²⁷ on the basis of conductance measurements.

It is clear from the spectra of *II* in benzene and in dichloromethane that, similar to compound *I* (ref.⁸), the signal of the α -methylene protons in benzene is shifted to lower fields and the signal of the β -methoxyl proton to higher fields as a result of decreased and increased shielding, respectively. In agreement with the literature¹⁶⁻¹⁹, it follows that, under the conditions in benzene solution the signals

of the methoxyl or β -methylene groups in the neighbourhood of solvating oxygen are shifted to higher fields. If the spectra of compounds *II* are compared from this point of view, it is seen that, in addition to the signal of the *Ib-2* methoxyl, the signal of complex *Ila-1* with *Ila-4*, with formal structure *Ila-3* or *Ila-2*, lies at higher field strengths. In complex alkoxyaluminates *I*, the lowest field region is occupied by the signals of methoxyl ($\delta = 3.34$ ppm) and β -methylene ($\delta = 3.68$ ppm) in the presence of the tetraethylammonium cation *Id*, where direct solvation of the cation is improbable²⁸. The alkoxy oxygen atoms can coordinate only with the aluminium atom, which has the highest coordination number, six^{7,29,30}. Six or eight oxygen atoms of *Id-2* or *Id-1* correspond to a maximum of two solvation sites and the remaining oxygen atoms cannot take part in solvation. The conditions in *Id* are probably further complicated by the ability of benzene to be localized in the vicinity of the voluminous tetraethylammonium cation. On the other hand, the signals of *Ia-3* with the lithium cation lie at substantially higher fields ($\delta_{\text{CH}_3} = 3.07$ ppm, $\delta_{\beta\text{-CH}_2} = 3.12$ ppm); in this substance, one lithium atom corresponds to only four oxygen atoms. The interaction between oxygen and the cation during coordination is apparently strongest for lithium, which can be an acceptor for four oxygen atoms^{19,20}.

In addition, two solvation positions on the aluminium atom are available for the 2-methoxyethoxyl oxygen atoms.

It can be assumed for hydridoalkoxoborate *Iib-2*, on the basis of the measured NMR spectra and the above considerations that: 1) All three 2-methoxyethoxyl β -oxygen atoms are coordinated to the sodium atom (the chemical shifts of the methoxyl and β -methylene groups of alkoxy *Iib-2* correspond to the chemical shifts of *Ib-2*). 2) At least some of the three α -oxygen atoms are coordinated to the sodium atom. In *Iib-2*, the chemical shift of the α -methylene group corresponds to the chemical shift in series *I* and *II*, except for *Id*, where oxygen-tetraalkylammonium coordination is practically non-existent²⁸. In solvents other than benzene (*e.g.* in dichloromethane) the protons of the α - and β -methylenes yield only one relatively narrow multiplet suggesting similar bonding conditions at both 2-methoxyethoxyl oxygen atoms.

It should be added that the special arrangement of the 2-methoxyethoxyl ligands in solvation of sodium² or aluminium⁷ is reminiscent of cryptate, except that here the cyclic bonds are not limited to optimum approach to the cation, and the signal of the solvating alkoxy proton of compound *IV* appears at higher field strengths⁷.

Thus it cannot be excluded that, in compounds *I* and *II*, a shift of the proton signal occurs in the vicinity of oxygen bonded to sodium or aluminium, with formation of a cryptate structure.

The IR spectra of substances *Iib-2* and *Ib-2* in the 800–1400 cm^{-1} region, *i.e.* the region of valence vibrations of the C—O and C—O—C bonds (Fig. 2, Table II) are very similar. *Iib-2* exhibits more intense bands than *Ib-1* at higher wavelengths

TABLE II

Wavelengths (cm^{-1}) of the Bands in the IR Spectra of Sodium Monohydrido-tris(2-methoxyethoxy)aluminate (*Ib-2*), Sodium Monohydrotris(2-methoxyethoxy)borate (*Iib-2*) and Sodium Tetrakis(2-methoxyethoxy)borate (*Iib-1*) in the 800–1500 cm^{-1} Region
vs very strong, s strong, w weak, vw very weak, br broad, sh shoulder.

<i>Ib-2</i>	<i>Iib-2</i>	<i>Iib-1</i>
841 s	841 w	838 w
	860 sh	879 vw
928 vs		924 sh
958 sh	961 s, br	
983 sh		993 vs
1 028 s	1 030 s	1 020 sh
		1 040 sh
1 090 vs	1 078 vs	1 090 vs
		1 105 sh
1 120 sh, br	1 128 sh, br	1 131 sh
1 200 s	1 201 s	1 201 w
1 249 s	1 248 w	1 248 w
1 290 w	1 285 w	1 285 vw
1 225 vw	1 335 vw	
1 369 s	1 370 s	1 371 vw
1 396 w	1 390 vw	1 405 vw
1 458 vs	1 455 s	1 458 w

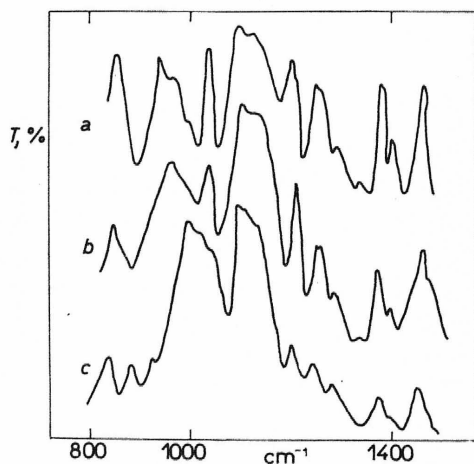


FIG. 2
The 800–1500 cm^{-1} Region of the Spectra of *a* Sodium Monohydrido-tris(2-methoxyethoxy)aluminate, *b* Sodium Monohydrotris(2-methoxyethoxy)borate and *c* Sodium Tetrakis(2-methoxyethoxy)borate

only in the $900-1000\text{ cm}^{-1}$ region, indicating a much lower content of coordinating oxygens^{10,31}. Complex *Iib-1*, for which the $^1\text{H-NMR}$ spectrum also indicated a lower content of coordinating alkoxy oxygens, is polymeric and thus apparently has a different structure. Similarly, the position and character of many bands in the IR spectrum of complex *Iib-1* differ from that of both *b-2* compounds (Fig. 2, 3, Table II).

The results of measurement of the molecular weights, IR, $^1\text{H-}$ and $^{11}\text{B-NMR}$ spectra of compounds *I* and *II* indicate that sodium monohydro-tris(2-methoxyethoxy)borate (*Iib-2*) has structure *VI* (Fig. 4). If the boron atom in this structure is replaced by an aluminium atom and the possibility of bond formation between the uncoordinated oxygen in the α -position of the alkoxy and aluminium is considered, then structure *VI* changes to structure *V*.

The distance between the boron atom and each sodium atom, using a model of structure *VI*, was found to be approximately 0.28 nm ; Marezio³² found an Na-B

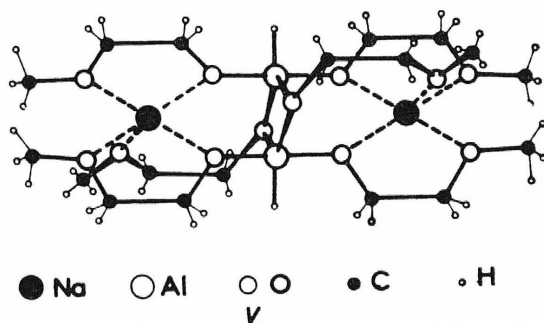


FIG. 3

The Structure of Sodium Monohydro-tris(2-methoxyethoxy)alumininate (*Ib-2*)

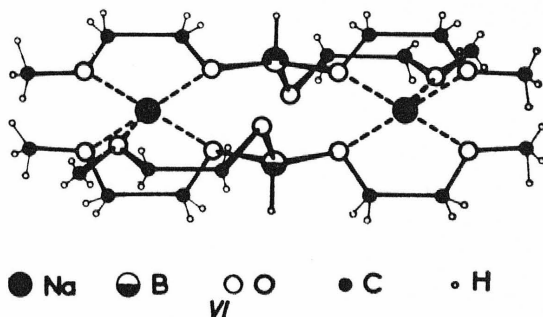


FIG. 4

The Structure of Sodium Monohydro-tris(2-methoxyethoxy)borate (*Iib-2*)

bond length of 0.272 nm on the basis of X-ray diffraction of crystalline NaBO_2 and Soldate³³ assumed an Na—B bond length of 0.307 nm in crystalline NaBH_4 . However, it must be assumed that structure of dimeric sodium monohydro-tris(2-methoxyethoxy)borate also involves coordination between the free alkoxy α -oxygen and the sodium atom and simultaneous destruction of the coordination between this sodium and an oxygen atom of alkoxy on another boron atom. Similarly, the existence of four and six-coordinated sodium cannot be excluded, although model structure VI involves the least tension.

EXPERIMENTAL

Chemicals

Compounds I—III were prepared in the same manner as in the previous works^{3,6,34}. All reactions and spectroscopic measurements were carried out in a dry nitrogen atmosphere. The solvents used were distilled from a sodium dihydro-bis(2-methoxyethoxy)aluminate solution immediately before use. Molecular weights were found ebullioscopically in benzene solutions or cryoscopically in the manner described in an earlier work⁶.

Spectroscopic Measurements

The ¹¹B- and ¹H-NMR spectra of benzene, toluene, dichloromethane and dioxane solutions were measured on a Varian XL-100-15 instrument at 32.1 MHz and at 100.1 MHz using the methyl ester of boric acid and tetramethylsilane as internal standards. The infrared spectra were measured on a Beckman IR 20A spectrometer as a film between KBr windows, as the substance or as a 15% suspension of the sample in perfluorkerosene and in Nujol, or as a 5% solution in benzene.

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