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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

IV. NMR SPECTRA OF ORGANOTIN COMPOUNDS

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SUMMARY

Del Re calculations have been extended to correlate and interpret the NMR data in the organotin compounds. The methyl proton chemical shifts have been correlated with the partial charge on the methyl hydrogen atom. Variations in ^{13}C–H and tin–proton coupling constants have been correlated with the calculated Coulomb integral values, and the relationship has been interpreted in terms of the change in the *s*-character of the appropriate atomic orbital using isovalent hybridisation arguments in conjunction with the calculated theoretical quantities.

INTRODUCTION

NMR spectroscopy has been widely used in the study of organotin compounds. The volume of published data on proton chemical shifts, tin–proton spin–spin coupling constants and ^{13}C–H spin–spin coupling constants etc. in organotin compounds is considerable and comprehensive compilations are available[1–3]. Although there have been several discussions of the factors influencing chemical shifts[4–7], tin–proton spin–spin coupling constants[8–10] and ^{13}C–H spin–spin coupling constants[11,12], there has been no general correlation of these quantities with theoretically significant parameters, such as partial charges on the nucleus. We have therefore, attempted to systematize and correlate the various NMR data on organotin compounds in terms of partial charges and Coulomb integral parameters calculated by the Del Re method.

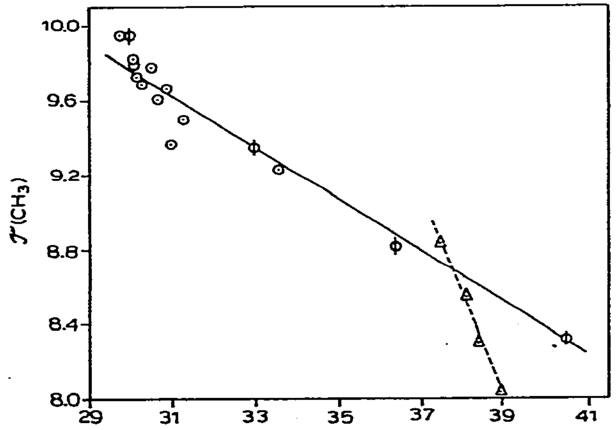
RESULTS AND DISCUSSIONS

(*A*). *Proton chemical shifts of organotin compounds*

It has been shown[13] that proton chemical shifts can be correlated with the electron density or the partial charge on the hydrogen atom provided the other factors influencing the chemical shifts, *viz.*, neighbour anisotropy effects, ring current effects, etc., are either absent or remain constant within the group of compounds being studied.

Since unsaturated and aromatic groups are known to exert appreciable anisotropy and ring current effects, the present study is restricted to methyltin compounds only. The partial charges on the methyl protons calculated by using the previously reported Del Re parameters[14,15], are given in Table 1 along with the reported chemical shifts[1-3] [$\tau(CH_3)$] for a number of alkyltin compounds, and the correlation is shown in Fig. 1. In view of the large solvent dependence of the proton chemical shifts[4], and consequent uncertainty in $\tau(CH_3)$, the correlation is fairly good. It is interesting to note that values of $\tau(CH_3)$ in the ethyltin compounds are lower than would be expected from the straight line shown in Fig. 1. This is consistent with the conclusion by Drago and Matwiyoff[11,12] that large anisotropic contributions to the proton chemical shifts exist in the organotin compounds. Since the methyl protons in the ethyltin compounds are further removed from the tin atom than they are in the methyltin compounds, the shielding due to the anisotropic effect of the tin atom will be less in the ethyltin compounds, leading to lower $\tau(CH_3)$ values. This conclusion is further supported by the existence of another linear correlation between $\tau(CH_3)$ and $q(H)$ for the ethyl series (shown by the dashed line in Fig. 1), since the anisotropic effect, although different from that in the methyl series, remains constant within the series because of the identical disposition of the methyl groups.

An interesting NMR parameter that has often been used in the study of the ethyl compounds is the difference in the chemical shifts between methyl and methylene protons [$\tau(CH_3)-\tau(CH_2)$], and an approximately linear correlation between $\Delta\tau$ and the electronegativity of the substituent X in the series C_2H_5X has been established[16-18]. Although the substituent atom, X, has been varied in all these studies, variations in $\Delta\tau$ will occur even when X remains the same, depending on the other groups attached to it, as is evident from the data given in Table 2. This is because the actual electronegativity of the substituent atom will depend on its environment, owing to the variations in the effective nuclear charge[14] (the Pauling or other electronegativities assigned to an element refer to some standard compound of the element). Since there is no established method for estimating such electronegativities, the Cou-



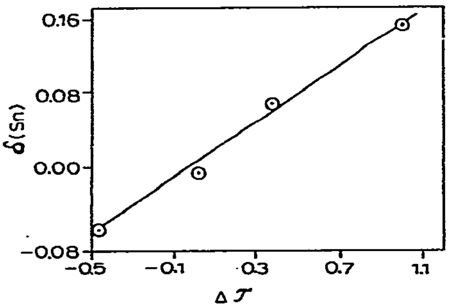


Fig. 1. Correlation between the partial charge $q(H)$ and chemical shift of methyl hydrogen $\tau(CH_3)$ of some organotin compounds (⊙, methyltin compounds; △, ethyltin compounds).

Fig. 2. Correlation of the Coulomb integral $\delta(Sn)$ with $\Delta\tau(\tau(CH_3)-\tau(CH_2))$ of the series $(C_2H_5)_nSnCl_{4-n}$.

TABLE 1

CALCULATED PARTIAL CHARGES q(H), FOR THE METHYL PROTONS, AND CHEMICAL SHIFTS, $\tau(CH_3)$, IN SOME ORGANOTIN COMPOUNDS

Compound	$q(H)$	$\tau(CH_3)$
$(CH_3)_4Sn$	0.0300	9.90–9.96
$(CH_3)_3SnCl$	0.0330	9.34–9.39
$(CH_2)_2SnCl_2$	0.0364	8.76–8.85
CH_3SnCl_3	0.0405	8.31–8.35
$(C_2H_5)_4Sn$	0.0375	8.80–8.85
$(C_2H_5)_3SnCl$	0.0381	8.55
$(C_2H_5)_2SnCl_2$	0.0384	8.30
$C_2H_5SnCl_3$	0.0389	8.04
$(CH_3)_2Sn(CF_2CF_2H)_2$	0.0310	9.37
$[(CH_3)_3Sn]_2CH_2$	0.0298	9.94
$(CH_3)_3SnH$	0.0301	9.82
$(CH_3)_2SnH_2$	0.0301	9.80
CH_3SnH_3	0.0302	9.73
$(CH_3)_3SnCF_3$	0.0307	9.61
$(CH_3)_2SnCF_3Cl$	0.0336	9.23
$(CH_3)_3SnCCl_3$	0.0313	9.50
$(CH_3)_2SnH(CF_2CF_2H)$	0.0303	9.69
$(CH_3)_3SnCHCl_2$	0.0309	9.66
$(CH_3)_3SnCH_2Cl$	0.0305	9.78

TABLE 2

THE CALCULATED COULOMB INTEGRAL VALUES FOR THE TIN ATOM AND $\Delta\tau$ $[\tau(CH_3)-\tau(CH_2)]$ IN THE SERIES $(C_2H_5)_nSnCl_{4-n}$

Compound	$\delta(Sn)$	$\Delta\tau$	*Ref.*
$(C_2H_5)_4Sn$	−0.0598	−0.468	2
$(C_2H_5)_3SnCl$	0.0029	0.034	
$(C_2H_5)_2SnCl_2$	0.0759	0.366	
$C_2H_5SnCl_3$	0.1617	0.990	

lomb integral parameter δ(X) of the atom X may be considered to be a very good measure of its true electronegativity in the compound being examined, because the standard Coulomb integral parameter, δ^0(X), is given by relation (1), in which X(X)

$$\delta^0(X) = k\cdot[X(X)-X(H)] \tag{1}$$

and X(H) are the standard electronegativities of X and hydrogen, and k is a proportionality constant. The experimental justification for this assumption is provided by the linear correlation between $\Delta\tau$ and δ(Sn) for the ethyltin compounds (Table 2 and Fig. 2). The utility of this postulate will be further demonstrated below.

(*B*). ^{13}C–*H spin–spin coupling constants in organotin compounds*

It has been shown that Fermi contact interaction is the dominant term in the spin–spin coupling interactions between two nuclei[13]. Using the Valence Bond model, the magnitude of ^{13}C–H coupling constants can be interpreted in terms of (*i*) the effective nuclear charge of the carbon atom, and (*ii*) the *s*-character in the orbitals used by the carbon atom to bond the hydrogen atom[19-21]. The dependence of $J(^{13}C\text{–}H)$ on these factors is expressed quantitatively by relation (2), in which Z_{eff} is the effective

$$J(^{13}C\text{–}H) = A \cdot Z_{eff}^3 \cdot \rho_s \qquad (2)$$

nuclear charge, ρ_s is the *s*-character of the carbon orbitals used to bond the hydrogen atom, and A is a constant involving gyromagnetic ratios, mean excitation energy, Planck's constant etc.

It is generally believed that the variations in $J(^{13}C\text{–}H)$ are primarily due to changes in the *s*-character of the carbon orbital[11,12,19,20], although this view has been strongly criticised recently[21]. Since the Del Re calculations offer some scope for estimating contributions of the various factors influencing the magnitude of $J(^{13}C\text{–}H)$, this point will be now examined in some detail.

Firstly, consider the series Me_nMCl_{4-n}, where M is carbon or tin, on which we have carried out Del Re type calculations. Because of the success of the Del Re calculations in correlating diverse physical properties including dipole moments and bond polarities in organotin compounds[14,15,22], the partial charges calculated by this method appear to be quite reliable. Using eqn. (7) of our previous paper[14], together with the calculated partial charges on the carbon atom, it is possible to obtain the effective nuclear charge, Z_{eff}, for the methyl carbon atom in the various compounds. The results are shown in Table 3, along with the reported values of $J(^{13}C\text{–}H)$. The data given in the last column have been calculated on the basis of eqn. (2), using $(CH_3)_4C$ as reference compound to show the expected changes in the magnitude of $J(^{13}C\text{–}H)$ resulting from the change in Z_{eff} alone. It is clear that variation in Z_{eff} can account for only a very small fraction of the total change, and may even be neglected in most cases. The results are consistent with the view that $J(^{13}C\text{–}H)$ is primarily determined by the changes in *s*-character of the carbon orbital.

In order to examine whether the changes in the *s*-character of the carbon orbital can correlate $J(^{13}C\text{–}H)$ data, isovalent hybridization arguments[23] may be applied. Isovalent hybridization arguments indicate that as X becomes more electrone-

TABLE 3

EFFECTIVE NUCLEAR CHARGE OF METHYL CARBON AND C^{13}–H COUPLING CONSTANTS IN THE SERIES $(CH_3)_nMCl_{4-n}$ (M = C or Sn)

Compound	*q(C)*	$Z_{eff.}$	$J(^{13}C\text{–}H)$(Hz)	
			Exptl.	*Calcd.*
$(CH_3)_4C$	−0.1191	3.208	124.0	124.0
$(CH_3)_3CCl$	−0.0976	3.216	127.0	124.9
$(CH_3)_2CCl_2$	−0.0726	3.225	131.8	126.0
CH_3CCl_3	−0.0433	3.235	124.2	127.2
$(CH_3)_4Sn$	−0.2500	3.162	128.0	118.8
$(CH_3)_3SnCl$	−0.2053	3.178	133.0	120.6
$(CH_3)_2SnCl_2$	−0.1537	3.196	137.8	122.7
CH_3SnCl_3	−0.0935	3.217	143.0	125.0

TABLE 4

CALCULATED COULOMB INTEGRAL VALUES δ(M) FOR THE SUBSTITUENT ATOM M(C or Sn) AND ^{13}C–H COUPLING CONSTANTS IN SOME METHYLTIN AND METHYLCARBON COMPOUNDS

Compound	$\delta(M)$	$J(^{13}C\text{–}H)(Hz)$	*Ref.*
$(CH_3)_4C$	0.1214	124	
$(CH_3)_3CCl$	0.1979	127	
$(CH_3)_2CCl_2$	0.2867	131.8	
CH_3CCl_3	0.3907	134	
$CH_3\text{–}CH_3$	0.1294	126	
CH_3CH_2Cl	0.2271	128	4, 26
CH_3CHCl_2	0.3134	131	
$(CH_3)_4Sn$	−0.0600	128	
$(CH_3)_3SnCl$	0.0032	133	
$(CH_3)_2SnCl_2$	0.0764	137.8	
CH_3SnCl_3	0.1624	143	

gative in the compound Y–A–X, more *p*-character is employed in the A–X orbital, and there is a corresponding increase in the *s*-character in the A–Y orbital. Thus, in the series $(CH_3)_nMX_{4-n}$, the *s*-character in the C–H bond of the methyl group will increase in proportion to the electronegativity of the central element M. Since the Coulomb integral parameter, δ(M), has been shown to be a good measure of the electronegativity of M, a linear correlation between $J(^{13}C\text{–}H)$ and δ(M) may be expected if the change in the *s*-character in the C–H bond is the dominating factor. The data given in Table 4, and the correlation shown in Fig. 3, confirm this view. Significantly, two separate straight lines are obtained, one for the carbon compounds and another for the tin compounds, indicating that the *s*-character in the C–M bond is determined both by the nature of the element M and by its electronegativity. Although this effect was not considered by Bent[23] in the development of isovalent hy-

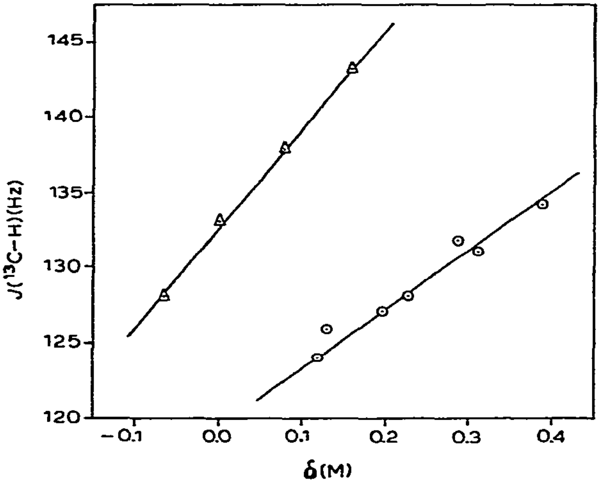


Fig. 3. Correlation of the Coulomb integral δ(M) for the substituent atom M (M = C or Sn) with $J(^{13}C\text{–}H)$ in some methyltin and methylcarbon compounds [△, methyltin compounds; ⊙, methylcarbon compounds].

bridisation schemes, it is to be expected, since the hybridisation at the carbon atom in the system H_3C–M will depend both on the relative electronegativities of hydrogen and M and on the overlap between the carbon hybrid orbitals and those of hydrogen and M, the latter being determined by the shape and size of the valence orbital of M. A case in point is the $J(^{13}C–H)$ data for the compounds $(CH_3)_4C$ and $(CH_3)_4Sn$. On the basis of electronegativity alone, the *s*-character in the C–H bond in $(CH_3)_4C$ would be expected to be larger than that in $(CH_3)_4Sn$, and consequently $J(^{13}C–H)$ in $(CH_3)_4C$ should be greater than $J(^{13}C–H)$ in $(CH_3)_4Sn$, although the reverse order is observed. In fact, for all the compounds of the series $(CH_3)_nMCl_{4-n}$ (M=C or Sn), although δ(Sn) is always less than δ(C) in the corresponding compound, $J(^{13}C–H)$ is consistently higher for the tin compounds indicating that the *s*-character of the carbon hybrid orbital used in the C–H bond and thus the *p*-character in the C–Sn orbital is higher than would be expected from electronegativity alone. An important conclusion from this is that the electronegativity of a substituent atom or a group is not the only factor influencing the hybridisation, and various other factors such as interatomic overlap etc. must be taken into account.

(*C*). *Tin–proton spin–spin coupling constants*

The indirect tin–proton spin–spin coupling constants for the methyltin compounds have been studied by several investigators[8,10,24,25] because of their importance in the elucidation of molecular structure. As in the case of $J(^{13}C–H)$, the magnitude of the tin–proton coupling constants may be interpreted in terms of the effective nuclear charge on the tin atom and the *s*-charactor in the tin orbital used to bond to the methyl carbon atoms.

The role of the variations in the effective nuclear charge of the tin atom on tin–proton coupling constants has been investigated by using a method similar to that employed in the case of the ^{13}C–H coupling constant, and the results for the series $(CH_3)_nSnCl_{4-n}$ are shown in Table 5. They indicate that the variations in the tin–proton coupling constants expected because of changes in the effective nuclear charge of the tin atom are insignificant compared with the large observed variations, which must therefore be due to changes in the *s*-character in the tin–carbon bonds, as already suggested by other studies[8–10].

To examine the possibility of correlating quantitatively the tin–proton coupling constants with the *s*-character in the tin carbon bond, we consider the compounds

TABLE 5

EFFECTIVE NUCLEAR CHARGE ON THE TIN ATOM, AND TIN–PROTON COUPLING CONSTANTS, IN THE SERIES $(CH_3)_nSnCl_{4-n}$

Compound	*q(Sn)*	$Z_{eff.}$	$J(^{119}Sn–C–H)$ (*Hz*)	
			Exptl.	*Calcd.*
$(CH_3)_4Sn$	0.6400	4.374	54.0	54.0
$(CH_3)_3SnCl$	0.7066	4.397	59.7	54.9
$(CH_3)_2SnCl_2$	0.7654	4.418	71.0	55.6
CH_3SnCl_3	0.8141	4.435	100.0	56.3

$(CH_3)_nSnX_{4-n}$ (the X's are not necessarily identical). Using the isovalent hybridisation argument, the increase in the p-character in the Sn–X orbital will be proportional to the electronegativity of X. In the light of our discussions in the previous section, the actual change in the electronegativity of the substituent X relative to tin will be proportional to $\delta(X)-\delta(Sn)$. Therefore, the total increase in the p-character in the tin orbitals used in all the Sn–X bonds is proportional to $\sum[\delta(X)-\delta(Sn)]$ where the summation is over all the bonds except the tin–methyl bonds. Since the increase in the p-character in the Sn–X bonds will result in an equal increase in the s-character in the tin–methyl bonds, the net increase in the s-character per tin–methyl bond ($\Delta\rho_s$), relative to that in $(CH_3)_4Sn$, will be given by relation (3), in which n is the number of

$$\Delta\rho_s = k\cdot\sum[\delta(X)-\delta(Sn)]/n \tag{3}$$

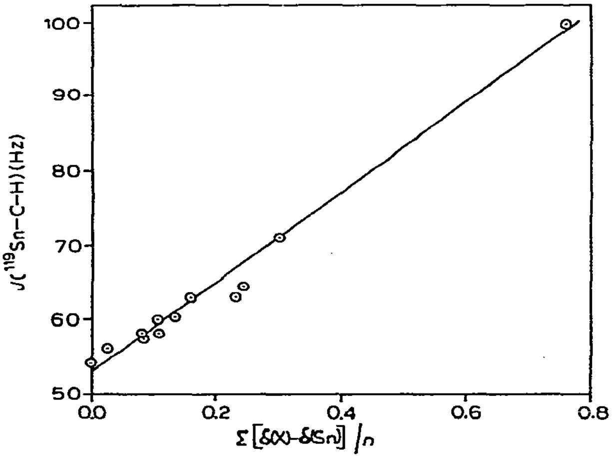
methyl groups bonded to tin and k is a proportionality constant. The total s-character in the bond will be given by eqn. (4), since the s-character in the tin–carbon bonds in

$$\rho_s = 0.25 + k\cdot\sum[\delta(X)-\delta(Sn)]/n \tag{4}$$

$(CH_3)_4Sn$ is 0.25 because of symmetry (sp^3 hybridisation at the tin atom). As the effective charge on the tin atom remains almost constant (Table 5), the tin–proton coupling constant, J(Sn–C–H), will be given by eqn. (5), in which B is a constant.

$$\begin{aligned} J(\text{Sn–C–H}) &= B\cdot\rho_s \\ &= 0.25B + k\cdot B\cdot\sum[\delta(X)-\delta(Sn)]/n \end{aligned} \tag{5}$$

It is clear from eqn. (5) that a linear relation between J(Sn–C–H) and $\sum[\delta(X)-\delta(Sn)]/n$ should exist if the variations in J(Sn–C–H) are due to the changes in the s-character in the tin–methyl bonds. The calculated values of the quantity $\sum[\delta(X)-\delta(Sn)]/n$ are given in Table 6 for a number of methyltin compounds. Fig. 4 shows the correlation between $\sum[\delta(X)-\delta(Sn)]/n$ and $J(^{119}$Sn–C–H). The linearity of the plot confirms the proposal[8–10] that the magnitude of J(Sn–C–H) is a measure of the s-



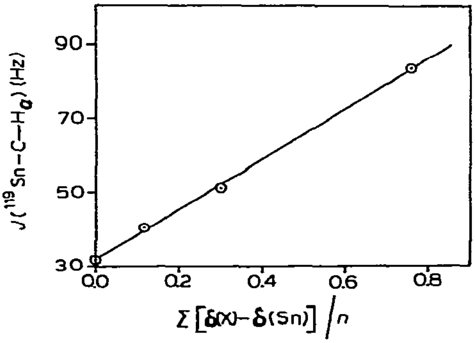


Fig. 4. Correlation between $\Sigma[\delta(X)-\delta(Sn)]/n$ and $J(^{119}$Sn–C–H) for some methyltin compounds.

Fig. 5. Correlation between $\Sigma[\delta(X)-\delta(Sn)]/n$ and $J(^{119}$Sn–C–H$_\alpha$) of some ethyltin compounds.

TABLE 6

VALUES OF $\sum[\delta(X)-\delta(Sn)]/n$ AND $J(Sn^{119}\text{–}C\text{–}H)$ IN SOME METHYLTIN COMPOUNDS

Compound	$\sum[\delta(X)-\delta Sn]/n$	$J(Sn^{119}\text{–}C\text{–}H)$ (*Hz*)	*Ref.*
$(CH_3)_4Sn$	0.0000	54.0	1, 2, 3, 27
$(CH_3)_3SnCl$	0.1160	59.7	
$(CH_3)_2SnCl_2$	0.3041	71.0	
CH_3SnCl_3	0.7578	100.0	
$(CH_3)_3SnH$	0.0272	56.5	
$(CH_3)_2SnH_2$	0.0799	58.0	
CH_3SnH_3	0.2361	63.4	
$(CH_3)_2Sn(CF_2CF_2H)_2$	0.2458	64.5	
$(CH_3)_2SnH(CF_2CF_2H)$	0.1625	62.8	
$(CH_3)_3SnCCl_3$	0.1323	60.3[a]	
$(CH_3)_3SnCHCl_2$	0.1089	58.3[a]	
$(CH_3)_3SnCH_2Cl$	0.0827	57.7[a]	

[a] These values have been calculated from the reported average values according to ref. 27.

TABLE 7

VALUES OF $\sum[\delta(X)-\delta(Sn)]/n$ AND $J(Sn^{119}\text{–}C\text{–}H_\alpha)$ IN SOME ETHYLTIN COMPOUNDS

Compound	$\sum[\delta(X)-\delta(Sn)]/n$	$J(Sn^{119}\text{–}C\text{–}H_\alpha)$ (*Hz*)
$(C_2H_5)_4Sn$	0	32.2
$(C_2H_5)_3SnCl$	0.1161	40.6
$(C_2H_5)_2SnCl_2$	0.3044	51.7
$C_2H_5SnCl_3$	0.7590	83.35

character in the tin orbital used to bond the methyl carbon atom. Although $J(^{119}Sn\text{–}C\text{–}H)$ data have been used in the correlation, a similar correlation exists with $J(^{117}Sn\text{–}C\text{–}H)$ also, because the ratio $J(^{117}Sn\text{–}C\text{–}H)/J(^{119}Sn\text{–}C\text{–}H)$ is constant.

A similar linear correlation exists between $\sum[\delta(X)-\delta(Sn)]/n$ and $J(Sn\text{–}C\text{–}H_\alpha)$ (α refers to the methylene (α) protons) in the ethyltin compounds. The relevant data are given in Table 7, and the correlation is shown in Fig. 5. Because of the considerable variation in the reported tin–proton coupling constants for the ethyltin compounds, all the data used in the present correlation have been taken from one source[2].

We conclude that, with some modifications and extensions, the Del Re method, despite the crude approximations involved in it, will prove to be a very valuable theoretical tool in the study of organotin compounds.

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