Methyl group librations in sterically hindered dimethylnaphthalene molecules: neutron diffraction studies of 1,8-dimethylnaphthalene between 50 and 200 K

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The structure of 1,8-dimethylnaphthalene has been studied by variable temperature single crystal neutron diffraction. The location of the two methyl groups on the same side of the naphthalene ring leads to substantial steric effects, notably a hindering of the methyl group librations. This steric effect appears to dominate over the alternative possibility of coupled motions of these groups. The results are compared directly with those from the related compound 1,5-dimethylnaphthalene where there is no possibility of methyl group coupled motions, but also less severe steric hindrance.

Introduction

Our recent work on variable temperature single crystal neutron diffraction using rapid data collection methods is aimed at changing the overall energy content of a system and monitoring the consequent structural changes. These can involve either the internal vibrations of the molecule, as indicated by anisotropic thermal parameters, or the order–disorder characteristics of parts of the molecule. Our neutron studies have included work on hydrogen atom migration[1] and ordering.[2,3] Also among these effects are torsional motions of librating terminal methyl groups,[4–6] and the influence of steric effects on these.[7] Both of these aspects are studied here.

Steric effects are an important factor in the stabilisation of molecular geometry in many systems. The "barriers" introduced are effective in defining conformation and stability. In sterically hindered situations the librations of a group are obviously constrained and the models describing such constrained librations must be substantially modified.

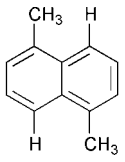
We have previously studied 1,5-dimethylnaphthalene[7] **1** in which a steric interaction between the methyl groups and the neighbouring hydrogen atoms on the same side of the naphthalene ring is likely to occur, reducing the propensity of the methyl groups to rotate freely in the crystal structure. The equilibrium orientation of the methyl groups in 1,5-dimethylnaphthalene was found to be essentially the same at all temperatures, with the in-plane hydrogen atom remaining in the plane even at 340 K, close to the crystal melting point. The torsional motions of the methyl groups were found to increase broadly with temperature, but the relatively low magnitude of these librations confirms that the groups are sterically hindered. The aim of the present work was to extend these measurements to the study of 1,8-dimethylnaphthalene, **2**, in which the equivalent steric clash is now between the methyl groups and therefore still more pronounced. The approach adopted here is to use the hydrogen atom atomic displacement parameters (ADPs) obtained from single crystal neutron diffraction as a means of monitoring the magnitude of the apparent methyl group torsional motions as the temperature increases.

The interpretation of the nature of methyl group motion in cases such as this where there are closely interacting methyl groups has for some time been a challenge; the tunnelling and NMR spectra are complex and difficult to interpret. The possibility exists for such closely coupled groups either to sterically hinder each other or to act co-operatively, for example by gearing their relative motions. In the present case of 1,8-dimethylnaphthalene (**2**) the methyl groups may have the potential to exhibit such coupled motions rather than static steric hindrance effects. If this were to be the case, clearly the data would give the opportunity to generate a modified description of the motion of coupled rotating groups, especially when compared directly with the motion of the methyl groups in sterically hindered 1,5-dimethylnaphthalene.

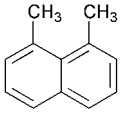
Experimental

Single crystal neutron diffraction data were collected from compound **2** at a series of temperatures, on the SXD instrument at the ISIS spallation neutron source.[4] Large single crystals were grown by repeated recrystallisation at *ca.* 5 °C from an acetone solution of **2** purchased from Aldrich Chemical Company, large single crystals appearing on the seventh recrystallisation. Since the samples are volatile, a crystal of dimensions 2.5 × 2.5 × 1 mm was sealed in a glass capillary and mounted in standard fashion on a Displex helium refrigerator. Initial data frames confirmed the unit cell and space group to be in agreement with the previous crystal structure determination of **2**.[8] Data sets were then collected at 50, 100, 150 and 200 K, along with a limited data set, from a second crystal, at 280 K (Table 1). At this final temperature the diffraction data clearly showed the crystal to be subliming during the experiment.

Refinement was carried out (on F^2) initially using GSAS,[9] and completed using SHELXL-93.[10] The details of the refinements are summarised in Table 1. The room temperature



1 (1,5-dimethylnaphthalene)



2 (1,8-dimethylnaphthalene)

Table 1 Summary of data collection and refinement parameters for 1,8-dimethylnaphthalene

Diffractometer	SXD neutron time-of-flight Laue diffractometer			
Detectors	Two, 64 × 64 element, 3 × 3 mm pixel, scintillator PSDs			
Detector position	Low angle: $2\theta_c = 55°$, $L_2 = 168$ mm, High angle: $2\theta_c = 126°$, $L_2 = 180$ mm			
Wavelength range/Å	0.5–5.0			
Formula	$C_{12}H_{12}$ 156.2			
Space group	$P2_1/c$			
Z	4			
T/K	50	100	150	200
a/Å	9.646(2)	9.678(2)	9.725(2)	9.773(2)
b/Å	6.904(2)	6.917(2)	6.938(2)	6.955(2)
c/Å	16.131(4)	16.141(4)	16.147(4)	16.158(5)
β/°	124.43(2)	124.39(2)	124.40(2)	124.36(2)
V/Å^3	886.1(4)	891.7(4)	898.9(4)	906.6(4)
D_c/g cm^{-3}	1.169	1.162	1.153	1.143
Observed reflections	2550	2788	1947	1566
Unique reflections [$I > 2\sigma(I)$]	1033	1297	751	596
R_{int}	0.065	0.062	0.077	0.091
Unobserved reflections	Not included in refinements			
μ/cm^{-1}	$1.08 + 1.00\lambda$			
$R(F)$	0.074	0.093	0.074	0.077
$wR(F^2)$	0.182	0.223	0.179	0.188
Goodness of fit (S)	1.097	1.190	1.074	1.132
Data/parameter ratio	4.8	6.0	3.5	2.7

crystal structure[8] was used as a starting model for the 100 K data set. The 50 and 150 K data sets were then refined using parameters from the 100 K refinement (Fig. 1a[11,12]) as starting models and finally the 200 and 280 K data sets were refined using parameters from the 150 and 200 K refinements, respectively, as starting models.

Owing to the low data:parameter ratios obtained from these poorly diffracting crystals, particularly at the higher temperatures studied, a careful refinement strategy was adopted to try to ensure the validity of the conclusions reached. This involved using rigid body constraints in the early stages of the refinement and comparing the parameters from these with those obtained in the final unconstrained refinements. The final refinements included 217 parameters. Table 1 shows the number of reflections and the final residuals for each refinement. While the data : parameter ratio is certainly lower than ideal in all cases, the refinement for the data sets from 50 to 200 K can be regarded as fairly reliable, especially given that the relevant parameters (for example, the ADPs of the methyl group hydrogen atoms and the geometry of this group) from the constrained refinements were found to be essentially the same as from the final unconstrained refinements. The 280 K data collected in this work were considered imprecise because of the limited data available and excluded from the subsequent analysis. The structure at 280 K will be determined at some future date using a recently developed novel multiple-crystal data collection method[1,13] which will minimise the data collection time and thus the effect of crystal sublimation.

CCDC reference number 440/219. See http://www.rsc.org/suppdata/nj/b0/b004123h for crystallographic files in .cif format.

Results and discussion

The refinements at all temperatures show that bond length C9–C1 is always greater than C1–C2 and C9–C8 is always greater than C8–C7 (see Table 2). This was previously found both in the X-ray study (in which the average value of C9–C1 and C9–C8 is 1.433 Å, whereas that of C1–C2 and C8–C7 is 1.363 Å) and in strain-energy minimisation calculations,[8] and indicates repulsion between the two methyl groups (Fig. 1b). Similar features were also found in the crystal structure of the

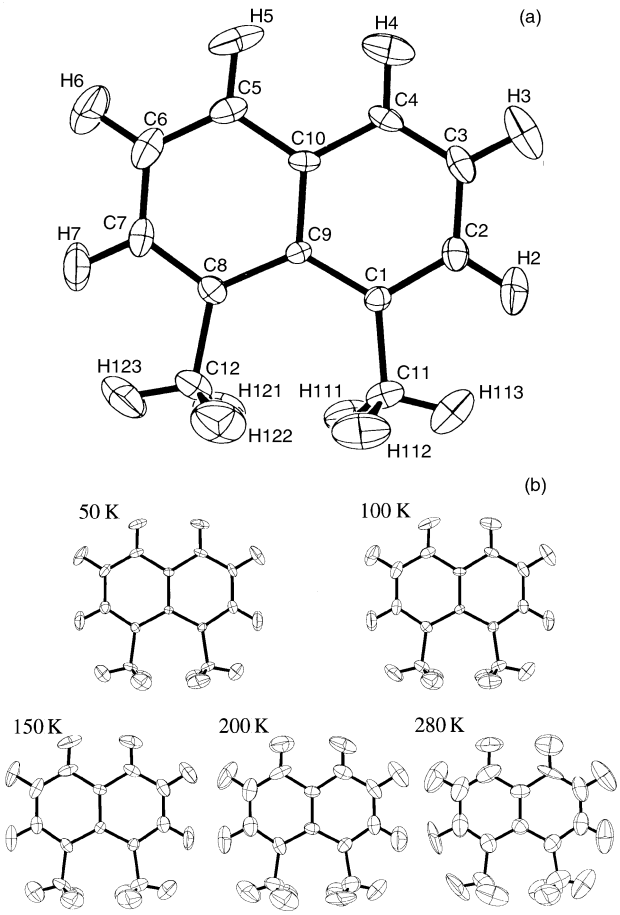


Fig. 1 (a) View of the 1,8-dimethylnaphthalene (**2**) molecule at 100 K, showing the atomic numbering used. Drawn using ORTEP[11,12] with thermal ellipsoids at 50% probability. (b) Evolution of the structure of 1,8-dimethylnaphthalene as a function of temperature (280 K data included purely for illustration). The repulsion of the two methyl groups is apparent in these plots, as is the general increase in the thermal parameters.

related compound 3-bromo-1,8-dimethylnaphthalene.[14] In the present study this feature is more apparent at higher temperatures. We also find here that the lengthening is not symmetrical about carbon C9; the difference between bond lengths C8-C9 and C8-C7 is always greater than the difference between C1-C2 and C1-C9 by approximately 0.04 Å. This may be attributed to local crystal environment effects. Further evidence that the methyl groups move apart to minimise steric hindrance is found, as expected, in the bond angles (see Table 2). C1–C9–C8, C9–C1–C11 and C9–C8–C12 are always greater than 120° (Fig. 1b), typically by about 5°; the opening of these angles is in good agreement with those found in the X-ray study[8] (in which the value of C1–C9–C8 is 125.2° and the average of C9–C1–C11 and C9–C8–C12 is 124.8°) and in related compounds.[14]

All methyl C–H bonds (apart from C11–H112 and C12–H122) decrease in length slightly as the temperature increases, consistent with the concomitant increase in the size of the ADPs. Most other bond lengths also decrease slightly as the temperature increases (from 50 to 200 K), again due to thermal effects. The ADPs of all atoms increase with temperature. This increase is greater for the carbon atoms than for the hydrogen atoms, reflecting the larger relative zero-point motion for the latter. The average proportional increase of the ADPs with temperature for the methyl hydrogen atoms is smaller than the corresponding value for the hydrogen atoms attached directly to the naphthalene ring, while that for the methyl carbon atoms is smaller than the corresponding value for the carbon atoms in the naphthalene ring.

The equilibrium orientation of both methyl groups remains the same at all temperatures with one hydrogen atom from each group always in the plane of the ring (Fig. 2). Indeed, the molecular framework as a whole remains planar in spite of the strain imposed on the ring by this steric effect. The same observation was made for 1,5-dimethylnaphthalene,[7] and this average geometry indicated by the crystallography suggests that steric hindrance will dominate over any possible co-operative gearing motions between these methyl groups. To confirm this a thermal motion analysis of these groups was carried out.

Thermal motion analysis

This was carried out using TLS analysis[15] of the refined ADPs (translation, liberation, screw) at each temperature using the program THMA11,[16] with the aim of characterising the apparent excess of torsional libration of the methyl groups about the C–C bonds connecting them to the naphthalene ring.[17] If a methyl group acts as a simple harmonic oscillator the libration of this group will behave as $\langle\phi^2\rangle = (RT/f) + \langle\phi_0^2\rangle$, where T is the temperature, R the gas constant and f the force constant. In this simple model the zero-point motion $\langle\phi_0^2\rangle$ results from the temperature independent internal modes.[17,18] Our work has assumed the simplest model, and has not taken into account the expected flattening off of the torsional motion at very low temperatures due to the increasing influence of these internal modes.[17] The residual zero-point motion estimated is thus a lower limit to the true value, but in practice the trend of $\langle\phi^2\rangle$ against T is so flat here that this is a very minor consideration. We note here that our

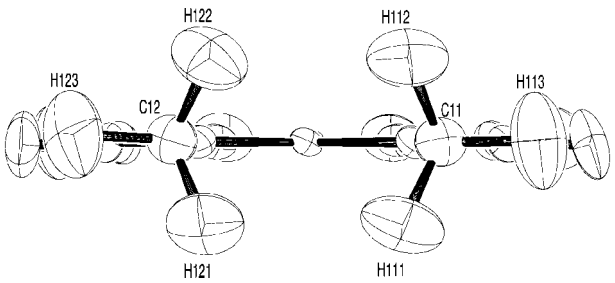


Fig. 2 View parallel to the ring plane in 1,8-dimethylnaphthalene at 100 K, showing the locked-in conformation of the methyl groups with a hydrogen atom of each group in the ring plane. This conformation is retained at each temperature studied.

Table 2 Bond lengths (Å) and angles (°) for 1,8-dimethylnaphthalene

	50 K	100 K	150 K	200 K
C1–C2	1.395(6)	1.397(7)	1.388(8)	1.389(12)
C1–C9	1.433(6)	1.438(6)	1.426(8)	1.440(12)
C1–C11	1.520(7)	1.512(7)	1.539(10)	1.532(15)
C2–C3	1.399(8)	1.408(8)	1.384(10)	1.388(15)
C2–H2	1.097(14)	1.097(14)	1.089(18)	1.11(3)
C3–C4	1.370(8)	1.376(8)	1.370(11)	1.371(15)
C3–H3	1.113(12)	1.090(13)	1.107(15)	1.13(2)
C4–C10	1.422(6)	1.424(7)	1.428(8)	1.412(13)
C4–H4	1.089(12)	1.086(13)	1.089(18)	1.06(3)
C10–C5	1.429(7)	1.421(7)	1.418(9)	1.451(14)
C10–C9	1.441(6)	1.440(6)	1.445(7)	1.428(11)
C9–C8	1.443(6)	1.444(6)	1.456(8)	1.441(12)
C8–C7	1.388(7)	1.384(7)	1.379(9)	1.367(15)
C8–C12	1.510(7)	1.515(7)	1.508(10)	1.499(14)
C7–C6	1.401(8)	1.399(9)	1.388(11)	1.406(17)
C7–H7	1.088(12)	1.087(12)	1.100(16)	1.13(3)
C6–C5	1.380(8)	1.378(8)	1.383(11)	1.369(16)
C6–H6	1.091(13)	1.082(14)	1.076(16)	1.05(3)
C5–H5	1.086(12)	1.097(13)	1.075(18)	1.09(3)
C11–H111	1.091(13)	1.097(12)	1.07(2)	1.09(4)
C11–H112	1.068(14)	1.086(15)	1.06(2)	1.08(3)
C11–H113	1.096(15)	1.077(15)	1.08(2)	1.01(4)
C12–H121	1.096(16)	1.089(15)	1.06(2)	1.09(4)
C12–H122	1.087(12)	1.070(14)	1.086(17)	1.10(3)
C12–H123	1.076(14)	1.084(15)	1.05(2)	1.04(4)
C2–C1–C9	119.3(4)	119.0(4)	119.6(5)	119.0(8)
C2–C1–C11	115.2(4)	115.5(4)	115.7(6)	115.1(9)
C9–C1–C11	125.5(4)	125.5(4)	124.8(5)	125.9(8)
C1–C2–C3	122.7(5)	123.1(5)	122.9(7)	123.1(9)
C1–C2–H2	117.6(8)	117.2(9)	116.9(10)	116.1(15)
C3–C2–H2	119.7(8)	119.6(8)	120.2(10)	120.8(14)
C4–C3–C2	119.5(4)	118.8(4)	119.7(6)	119.9(8)
C4–C3–H3	121.2(10)	121.0(11)	120.6(13)	120.8(19)
C2–C3–H3	119.3(10)	120.2(11)	119.6(12)	119.3(19)
C3–C4–C10	120.3(4)	120.8(4)	120.5(6)	119.1(9)
C3–C4–H4	120.2(8)	120.3(9)	121.1(10)	118.5(17)
C10–C4–H4	119.5(8)	118.9(9)	118.4(11)	122.4(17)
C5–C10–C4	118.1(4)	118.1(4)	118.2(6)	117.3(8)
C5–C10–C9	121.1(4)	121.2(4)	122.0(5)	120.2(8)
C4–C10–C9	120.9(4)	120.7(4)	119.9(6)	122.5(9)
C1–C9–C10	117.2(4)	117.6(4)	117.5(5)	116.4(7)
C1–C9–C8	125.2(4)	125.3(4)	126.0(5)	125.4(7)
C10–C9–C8	117.6(4)	117.1(4)	116.5(5)	118.2(8)
C7–C8–C9	118.9(4)	119.2(4)	118.6(5)	118.7(8)
C7–C8–C12	116.1(4)	116.3(4)	116.9(6)	115.7(9)
C9–C8–C12	125.0(5)	124.5(5)	124.5(6)	125.6(10)
C8–C7–C6	123.1(4)	123.1(5)	124.1(6)	124.0(9)
C8–C7–H7	119.3(9)	118.0(9)	118.7(11)	119.4(17)
C6–C7–H7	117.6(8)	118.9(9)	117.2(11)	116.6(18)
C5–C6–C7	119.9(5)	119.6(5)	119.6(6)	119.2(10)
C5–C6–H6	119.2(9)	119.8(11)	119.5(13)	118(2)
C7–C6–H6	121.0(9)	120.6(11)	120.8(12)	123(2)
C6–C5–C10	119.5(4)	119.9(5)	119.2(6)	119.6(10)
C6–C5–H5	121.9(8)	121.6(10)	122.9(11)	123.2(16)
C10–C5–H5	118.6(8)	118.5(9)	117.9(11)	117.1(16)
C1–C11–H111	113.6(8)	112.0(8)	112.1(11)	112.1(18)
C1–C11–H112	111.6(9)	113.1(9)	110.8(13)	109.3(18)
H111–C11–H112	108.7(11)	108.4(12)	108.6(16)	108(2)
C1–C11–H113	108.5(9)	109.0(10)	108.3(11)	111.2(18)
H111–C11–H113	105.5(15)	109.0(16)	108.7(19)	109(3)
H112–C11–H113	108.7(13)	105.0(15)	108.2(18)	107(3)
C8–C12–H121	112.1(8)	111.9(9)	111.5(10)	111.1(14)
C8–C12–H122	112.1(8)	112.4(9)	112.8(10)	113.7(16)
H121–C12–H122	109.0(13)	109.5(14)	109.1(15)	109(2)
C8–C12–H123	110.0(9)	110.1(10)	111.9(13)	114(2)
H121–C12–H123	108.4(12)	107.4(13)	107.1(14)	108(2)
H122–C12–H123	104.9(13)	105.2(13)	103.9(15)	102(2)

analysis of the methyl group torsional motions assumes these motions are in excess of those of the whole molecule. We are therefore relatively immune to the fact that the rigid body analysis undertaken in TLS ignores the internal molecular modes, which are known to be appreciable for the parent naphthalene molecule.[19]

The mean square amplitude of libration, $\langle\phi^2\rangle$, for both methyl groups (Fig. 3a) was found to be considerably smaller than the corresponding value for a methyl group undergoing relatively unhindered rotation, as observed in a molecule such as *p*-hydroxyacetanilide (paracetamol).[5,6] For example, $\langle\phi^2\rangle$ at 200 K for the methyl group in *p*-hydroxyacetanilide is approximately $650^{\circ 2}$, while the corresponding average value for the methyl groups in 1,8-dimethylnaphthalene is $168^{\circ 2}$. The slope of $\langle\phi^2\rangle$ and its value at higher temperatures for the methyl groups in 1,8-dimethylnaphthalene is also significantly smaller than for those in 1,5-dimethylnaphthlene (see Fig. 3b).

The severe effects of the intramolecular steric hindrance in compound **2** also mean that a clear temperature-dependent trend in the value of $\langle\phi^2\rangle$ is not apparent for either of the methyl groups (Fig. 3a). This confirms that the relationship $\langle\phi^2\rangle = (RT/f) + \langle\phi_0^2\rangle$ is inappropriate when the motion of the librating group is severely sterically hindered. Effectively the external influence of the neighbouring group makes the bond force constant have an unrealistically large apparent value. However, Fig. 3 still shows that significant zero-point motion is again evident, with extrapolation of the line of best fit to the average methyl group torsional motion yielding $\langle\phi_0^2\rangle = 118^{\circ 2}$. This determination of zero-point motion is unlikely to be precise, but it is similar to that of the freely rotating methyl group in *p*-hydroxyacetanilide ($\langle\phi_0^2\rangle = 121^{\circ 2}$)[5,6] and of that of the less sterically hindered methyl groups in 1,5-dimethylnaphthalene ($\langle\phi_0^2\rangle = 101^{\circ 2}$),[7] which are also shown in Fig. 3b. The close agreement of the residual zero-point motions of the librating methyl group in these various molecules gives added credence to our postulate that the intrinsic disorder or apparent thermal motion of hydrogen atoms in a crystal structure cooled close to absolute zero may be of a fairly constant magnitude.[20]

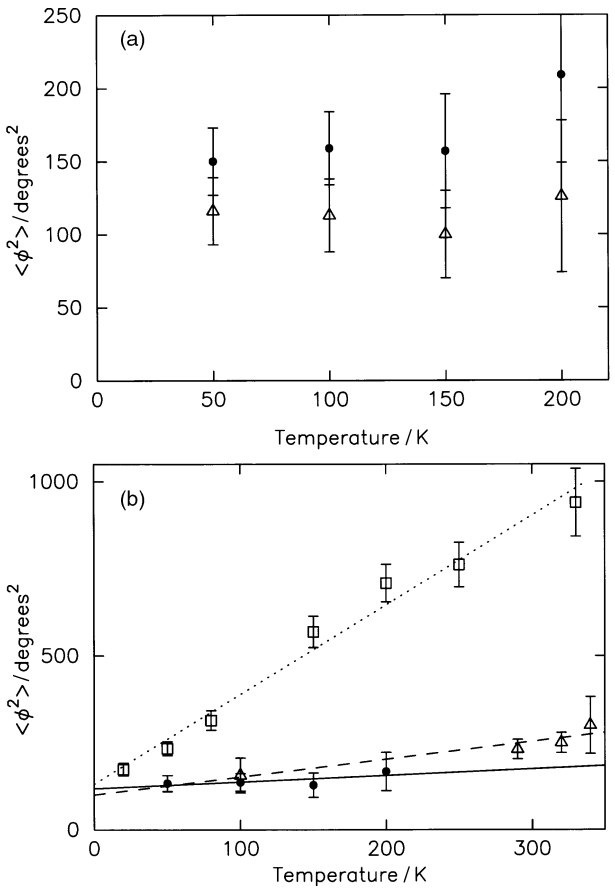


Fig. 3 (a) The methyl group torsional amplitudes $\langle\phi^2\rangle$ for the two methyl groups in 1,8-dimethylnaphthalene, as a function of temperature (solid circles, C11 methyl group; triangles, C12 methyl group). It is clear that there is no significant consistent increase of this parameter with temperature. (b) The methyl torsional motions in 1,5-dimethylnaphthalene[7] (triangles), paracetamol[5,6] (squares) and the average values in 1,8-dimethylnaphthalene (solid circles), along with linear fits to these (dashed, dotted and solid lines respectively). The convergence of the fits at an approximately constant value (around $\langle\phi_0^2\rangle = 110^{\circ 2}$) at $T = 0$ ("zero-point motion") is notable.

Conclusion

Our variable temperature neutron diffraction measurements of 1,8-dimethylnapthalene **2** have allowed us to confirm the features of the molecular geometry of this compound and postulate the presence of a large degree of steric hindrance at all temperatures. This in turn leads to a significant effect on the apparent methyl group librational motions, which are of considerably lower magnitude in this material than in many others studied, and also show no significant temperature dependence. It is of interest that even in this case where the methyl groups are heavily constrained in their apparent excess motion over the remainder of the molecule, the zero-point motion of this group is very similar to that found in other compounds.

Acknowledgements

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