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CRYSTAL STRUCTURE OF TRIPHENYL CYAMELURATE (2,5,8-TRIPHENOXY-1,3,4,6,7,9,9b- HEPTAAZAPHENALENE)

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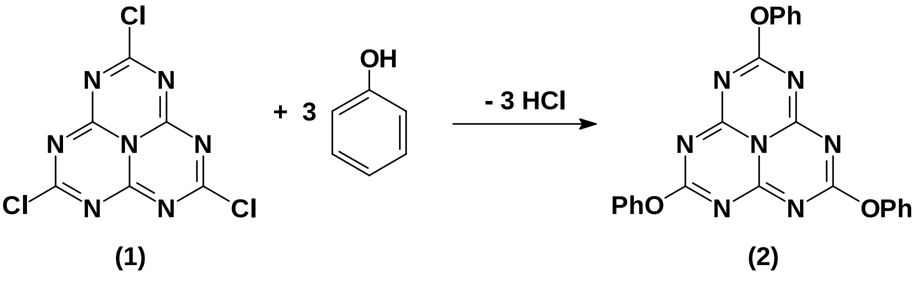
Abstract – 2,5,8-Triphenoxy-1,3,4,6,7,9,9b-heptaazaphenalene (triphenyl cyamelurate, $C_6N_7(OPh)_3$) was synthesized under solvent free conditions from cyameluric chloride ($C_6N_7Cl_3$) and phenol via nucleophilic substitution. Needle-shaped crystals were obtained via a vapor transport method. Single crystal XRD revealed that $C_6N_7(OPh)_3$ crystallizes in the monoclinic space group $\boldsymbol{P}\ 2_1/\boldsymbol{c}$ with the lattice parameters $\boldsymbol{a}$ = 14.463(17) Å, $\boldsymbol{b}$ = 4.697(3) Å, $\boldsymbol{c}$ = 31.60(4) Å and β = 99.76(9)°. All three phenyl rings are rotated and inclined differently with respect to the central heptazine units, which themselves form inclined stacks along the ***b*** axis. Intermolecular cohesion is provided via dipolar, aromatic and van-der-Waals interactions as well as some weak C–H···N and C–H···O hydrogen bridges.

INTRODUCTION

In recent years, an increased interest into compounds based on the tri-*s*-triazine or heptazine (C_6N_7) unit,[1] their structures and properties is documented by a number of publications. The C_6N_7 moiety, first postulated by Pauling and Sturdivant in 1937,[1] with its close resembly to the *s*-triazine unit C_3N_3 is considered an interesting building block for carbon nitrides.[2,3] In a first branch of this recent developement, the crystal structures of 'fundamental' heptazine-compounds $C_6N_7R_3$ that were already known before Pauling and some of which date back to the times of Liebig and Gmelin (see e.g. 3 and

References therein) were elucidated. Among these compounds are melem (R= NH_2)[4] and salts based on the cyamelurate (R = O^-)[5] and hydromelonate (R = NCN^-)[6] anion. The formation of melem and its de-ammination product melon were re-investigated thoroughly.[7] The latter is not to be considered a well-defined compound, rather than a mixture of –NH– bridged oligomeric and polymeric heptazine species in varying proportions. These proportions and the degree of crystalline order of melem depend on the synthesis conditions. In parallel, the high thermal stability and interesting electronic structure, the close analogy to the *s*-triazines and the estetic appearance of the C_6N_7 moiety prompted several researchers to carry out structural and other investigations on heptazine compounds that had been synthesized after Pauling and Sturdivant's correct allocation of the heptazine structure (R = H,[8] Cl,[3,9] NEt_2[10]) or had even been postulated by them, but remained unattended until recently (R = N_3; C_6N_{16}).[11] Furthermore, the tautomeric forms of cyameluric acid $C_6N_7(O_3H_3)$ have been studied experimentally[12] as well as theoretically.[13] Heptazine-based materials are suggested for various applications, especially flame retardents. Recently, a novel versatile non-hydrolytic sol-gel system based on C_6N_7 and silicon was discovered.[14] In this paper we report on the first structural characterization of a heptazine aryl ester, namely triphenyl-cyamelurate $C_6N_7(OPh)_3$ (**2**). The corresponding triazine-based aryl esters with the parent compound $C_3N_3(OPh)_3$ have been a matter of interest, because of their nonlinear optical properties.[15] The title compound was synthesized from trichloro-*s*-heptazine and phenol, in accordance to a recent publication on solvent free synthesis of *s*-triazine compounds (Scheme 1).[16]



Scheme 1: Synthesis of **2** via nucleophilic substition without solvent or aid-bases

While $C_3N_3(OPh)_3$ could be readily recrystallized from $CHCl_3$, recrystallisation of **2** from xylene yielded only microcrystalline powders. Colorless needles of sufficent size for single-crystal XRD were obtained via a vapor transport technique (see experimental part).

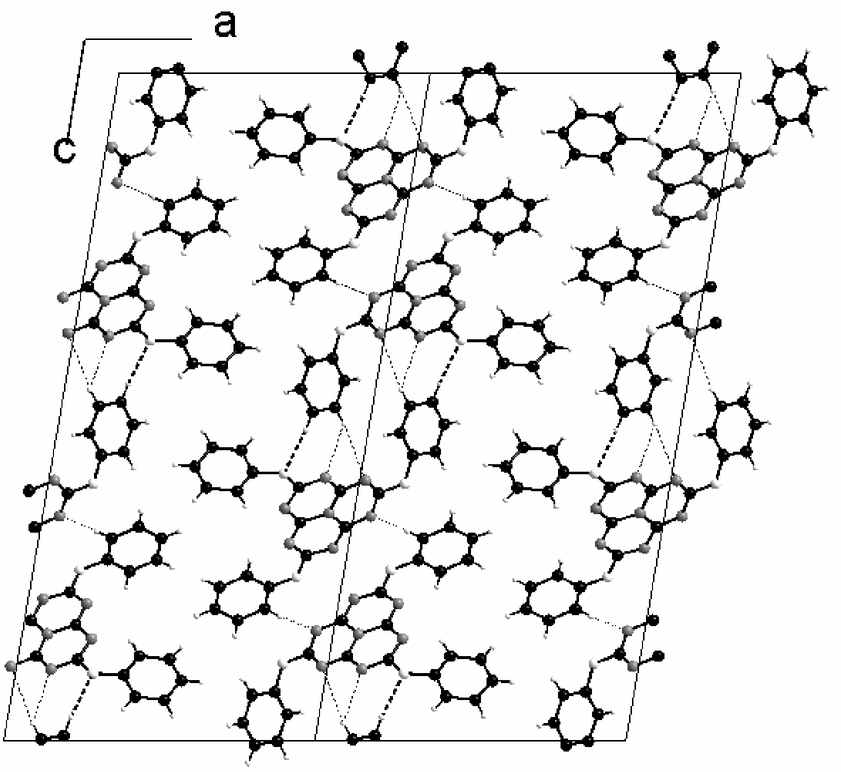


Figure 1: Projection of molecular arrangement of 2 into *a-c* plane, also showing N···H and O- -H hydrogen bonds.

RESULTS AND DISCUSSION

Figure 1 depicts a projection of two unit cells of **2** into the (101) plane, with the closest intermolecular N···H and O- -H distances, highlighted by dotted lines. In the direction perpendicular to the paper plane, the molecules are stacked and form infinite columns running parallel to the *b* axis. For clarity, hydrogen bonds connecting molecules within these stacks are not shown in Figure 1 and will be discussed further below (see Figure 3). In the ***a-c*** plane, each $C_6N_7(OPh)_3$ molecule is surrounded by six nearest neighbor molecules which are inversed with respect to the first one. It can be seen that the packing scheme of the molecules provides hydrogen bridging only along ***c***, whereas the intermolecular cohesion along ***a*** is obviously provided by van-der-Waals and π-interactions of the phenyl units. A detailed allocation of the atom numbers is given in Figure 2, along with the bond lengths. The lengths* of the N···H and O- -H contacts are 2.38 Å (H18···N3), 2.73 Å (H21···N2), 2.91 Å (H21···N7), and 2.77 Å (H22- -O1'), respectively (*error ≈ ±0.03 Å, see exp. part). This corresponds to relatively weak hydrogen bonds, which is to be expected from the low donor strength of the phenyl-H (Ph–H) atoms. The shortest hydrogen bond between N3 the H18 atom in *ortho* position has a close-to-straight Ph–H···N angle of ~172°, followed by Ph–H21···N2 (~142°) and Ph–H21···N7 (~136°). These bonds connect molecules *within each la*yer (as indicated by the double lines in Figure 2), whilst the H22- -O1' contact with a Ph–H- -O angle of 158.9° connects molecules *between consecutive layers*.

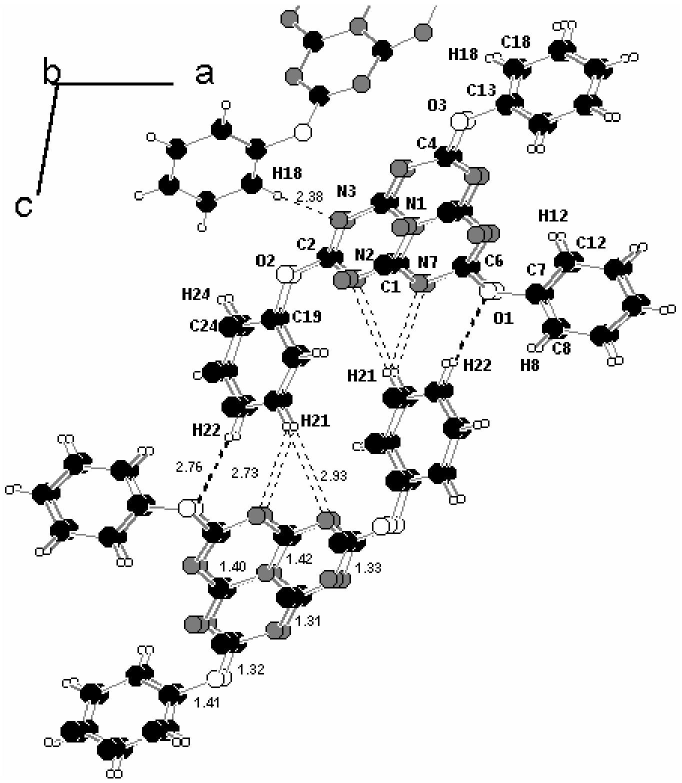


Figure 2: Detailed view of molecules from the center of Figure 1 with bond labels and assorted bond lengths.

As noted above, the molecules are stacked along the ***b*** axis. Stacking has also been observed in the corresponding triazine derivative $C_3N_3(OPh)_3$. In this case the C_3N_3 rings are oriented exactly perpendicular to the stacking direction and form so-called Piedford units (PUs). In contrary, the crystals of **2** contain the heptazine unit — and also the three phenyl rings — with different inclinations with respect to the stacking direction. The angle between the normal vector of the heptazine unit and the column axis is ~47.5°. This 'inclined stacking' is obeserved in several heptazine compounds. $C_6N_7(NEt_2)_3$ for example, shows a stacking scheme that is very similar to that of **2** and the angle of the heptazine unit and the column axis in this case is ~46.86°. Other examples with an inclined stacking are the cyamelurates $M_3[C_6N_7O_3]$ with M = Li, Na, and the melemium salts $C_6N_7(NH_2)_3 \cdot H_3PO_4$ and $(HC_6N_7(NH_2)_3)ClO_4 \cdot H_2O$.[17]

In Figure 3, two consecutive molecules in a column with the heptazine unit oriented parallel to the paper plane are shown. The overlap of the aromatic rings in this orthogonal projection, represented by the shaded area ("orthogonal overlap"), is comparatively small, approximately 1/3 triazine ring. The reason for this is that the aromatic π stacking is in competition with several other forces. First, there is the sterical demand of and attraction between the of the phenyl units. They are oriented parallel to each other and almost, but not entirely perpendicular to the central aromatic unit as in $C_3N_3(OPh)_3$. The distance between them, i.e. d1, d2 and d3 is 3.81, 3.83 and 3.39 Å, respectively, the latter of which is close to that of graphite (3.34 Å).

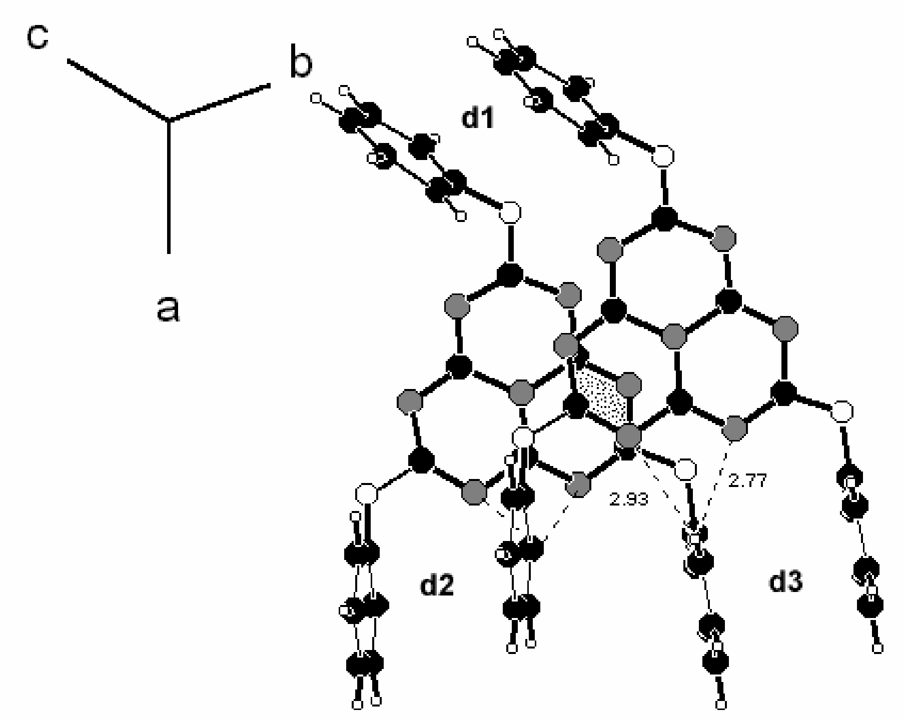


Figure 3: Two consecutive molecules in a stack. Shaded area represents overlap of aromatic rings.

Secondly, as already noted above, there are additional hydrogen bonds that provide intramolecular cohesion *along* the columns, but obviously also provide a contribution to the sidewards stepping arrangement of the molecules. They are formed between the ortho-hydrogens of the phenyl units and N5 and N6 of the molecule above and below (Figure 3). Finally, the negative partial charge at the nitrogen atoms prevents them from being stacked directly above one another. The heptazine units are instead translated sideward to form dipolar interactions between the positively polarized heptazine carbon atoms and the N and O atoms of the subsequent molecule. This situation is similar as in hexagonal boron nitride and has been observed in a large number of heptazine based crystals. However, it is also evident from Figure 3 that no atom is *exactly* above the other, which leads to different distances of these contacts, namely C4-N6 and C5-O1 (3.28 Å) and C3–N7 (3.20 Å), whereas the distance between the consecutive heptazine *planes* is 3.18 Å. This is small in comparison to other molecular and polymeric heptazine compounds. It appears that the heptazine moyeties can approach each other the closer, the less their triazine-rings overlap: 3.26 Å in $K_3[C_6N_7(N{=}C{=}N)_3]\cdot 5\,H_2O$ (> 2 rings), melem 3.27 Å (2 rings). Also triazido-heptazine $C_6N_7(NNN)_3$ fits into this pattern: The distance between subsequent heptazine planes is only 3.04 Å, however, there is virtually no orthogonal overlap as the C_6N_{16} molecules of sucessive layers A and B are arranged "on gap", so that the true distance between the heptazine units is twice as large, i.e. 6.07 Å. If this relationship is in deed valid, the number of overlapping rings in Melon (3.21 Å), which is so far unknown, should be between 1/3 and 2 rings. The comparatively larger distance of 3.34 Å in $C_6N_7(NEt_2)_3$. in spite of the fact that it has almost no overlap of the triazine rings, could be due to the sterically more demanding ethyl units. Like triphenoxy-triazine $C_3N_3(OPh)_3$, the compound $C_6N_7(NEt_2)_3$ has been found to exhibit interesting multipolar nonlinear optical properties and equivalent investigations with the title compound (**2**) are in preparation.

It is interesting to note that while $C_6N_{16} = C_6N_7(N_3)_3$ and its triazine counterpart $C_3N_3(N_3)_3 = C_3N_{12}$ show an almost perfect analogy in their crystal symmetry and molecular arrangements, (see Figure 7 in Ref. 6), in contrary, both the crystal structure of **2** and its molecular conformation are notably different from those of the corresponding triphenoxy-s-trazine $C_3N_3(OPh)_3$. In the crystal of **2** there is two types of columns each of which consists of molecules in a single configuration (the molecules in Figure 1 exactly cover the underlying ones), while the neighbour columns contain the molecule in inverse configuration (= 'antiparallel columns'). In the crystal of $C_3N_3(OPh)_3$, the neighbor molecules *within* a column are in inverse configuration and all columns are equal. Moreover, the triazine units are eclipsed with respect to each other but they are not inclined to the stacking direction. The distance between triazine units is ~3.3 Å, which is hence 0.1 Å larger than the closest C..N proximity within **2** (see above). A comparison of the bond length distribution between **2** and $C_3N_3(OPh)_3$ is shown in Figure 4. As can be seen, equivalent bond distances in both molecules roughly agree with one another, but no uniform trend between the heptazine and the triazine derivative can be observed.

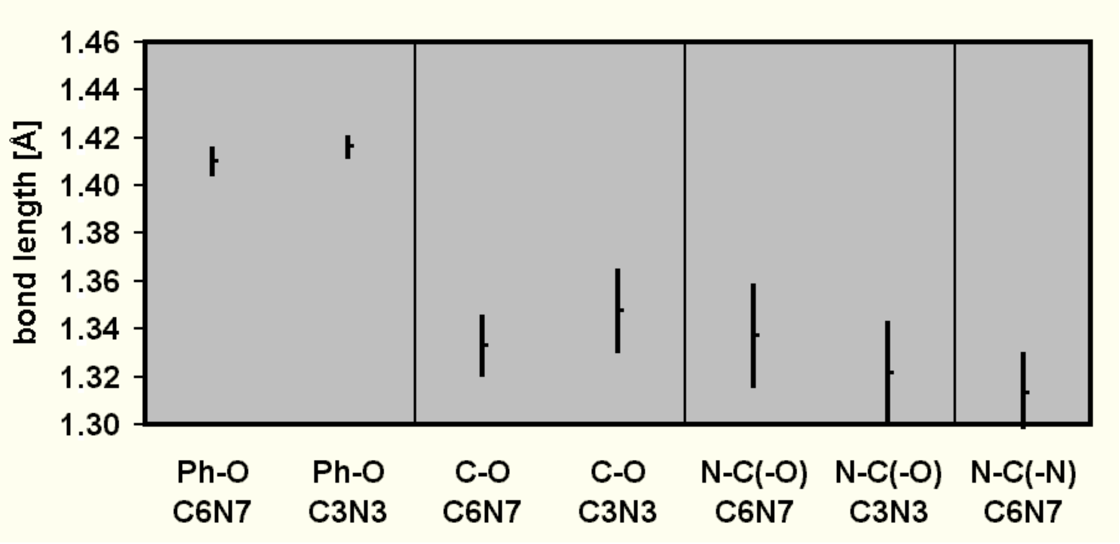


Figure 4: Comparison of maximum, minimum, and average bond lengths as observed in $C_6N_7(OPh)_3$ and $C_3N_3(OPh)_3$. Error (not shown) ≈ ± 0.03 Å

As previously noted, in **2** hydrogen bonding takes place *perpendicular* to the stacking direction with four non-equivalent hydrogen half-bonds per molecule (recall Figure 1). In contrary, in $C_3N_3(OPh)_3$ hydrogen bonding is *parallel* to the stacking direction. One ortho-hydrogen per phenyl unit is connected with the oxygen atoms of the neighbour molecule in the inverse conformation, producing a bonding pattern that conserves the D_3 symmetry of the molecular diad.

Table 1: Crystal data, measurement and structure refinement details for **2**

emp. formula	$C_{24}H_{15}N_7O_3$
formula weight	449.43
crystal system	monoclinic
space group	P 1 2_1/c 1 (Nr. 14)
a (Å)	14.463(17)
b (Å)	4.697(3)
c (Å)	31.60(4)
β	99.76(9)
V (Å^3)	2116(4)
Z	4
crystal shape	needle
cryst. dim. (mm)	1.00 × 0.06 × 0.02
$\rho_{calc.}$ (Mg/m^3)	1.411
ϑ (°C)	299(2)
radiation (Å)	MoK$_\alpha$; 0.71073
total no. of reflections	8535
no. of refine refl.	3852
no. of param.	307
h_{min} k_{min} l_{min}	(-17 -5 -39)
$h_{max}k_{max}$ l_{max}	(18 5 39)
R all	0.4411*
R gt	0.0440*
wR_2	0.0872
wR_2 gt	0.0533
GOF	0.498*

*see "Crystal Structure Determination of **2**"

EXPERIMENTAL

*Synthesis of 2,5,8-triphenoxy-1,3,4,6,7,9,9b- heptaazaphenalene, (triphenyl-cyamelurate) (**2**).*

A mixture of trichloro-*s*-heptazine ($C_6N_7Cl_3$) (1.02 g, 3.7 mmol) and phenol (4.00 g, 42.5 mmol) was stirred at 150°C in a Schlenk flask under Ar atmosphere. The yellowish melt was then further heated over an open flame for 1 h until the yellow colour had vanished. After removing excess phenol by distillation, xylene was added dropwise until the residue had been totally dissolved, while heating to 105°C. Several fractions of **2** were obtained by sucessive precipitation and filtration; 0.124 g (7.6%); mp 285°C; FT-IR(KBr, cm^{-1}): 691 (m), 740 (m), 816 (m); 1005 (w), 1026 (w), 1198 (s), 1260 (m), 1392 (vs), 1476 (w), 1485 (w); 1584 (w); 1593 (w), 1634 (vs), 2961 (vw), 3052 (vw), 3093 (vw), 3220 (w); MS (EI-FAB): m/z M$^+$ 449, M$^+$- OPh 356. Anal. Calcd for $C_{24}H_{15}N_7O_3$: C: 64.14; H: 3.36; N: 21.82. Found: C: 66.27(8); H: 3.54(7); N: 18.09(2).

*Crystallisation of **2***

The crystallization of **2** was accomplished by a vapor-transport method. Several 10 mg of **2** were filled in an open glass tube which was then introduced into a second, longer glass tube equipped with an electrical resistor coil for heating. The temperature at the locus of the sample was maintained close to the melting point of **2** while dry argon was purged through the tube furnace. Colourless needle-like crystals formed downstream outside the heated zone.

*Crystal Structure Determination of **2***

Diffraction data from a thin needle-shaped crystal (size 1000 µm × 60 µm × 20 µm) were collected with Mo-Kα radiation and a CCD SAPPHIRE2 detector in φ-scan mode on the Xcalibur system with the ENHANCE-X-ray source option from Oxford Diffraction.[18] The measurement had to be done at room temperature, because the stream of nitrogen coolant would have excited too strong mechanical vibrations of the thin needle. Previous attempts to prepare shorter needles by cutting perpendicular to the long axis led to too small fragments. Frame scaling was applied using the SCALE3 PACK command in CrysalisRed.[19] All observed reflections could be indexed, based on a primitive monoclinic cell, and 318 reflections have been considered for the refinement of cell parameters. SHELXS-97 and SHELXL-97 [20] have been used for structure solution and structure refinement, respectively. A stable structure model, establishing the molecular packing scheme discussed in this paper could already be obtained from 564 unique reflections with interplanar spacings $d_{hkl} \geq 1.68$ Å (R_{int}:R_σ = 0.131:0.111). Nevertheless, the residuals given in Table 1 were derived for a refinement down to $d_{\mathrm{hkl}} \geq 0.8$ Å. Reflections with $d_{hkl} \leq 1.3$ were low in intensity and added only little information, thus affecting the R_{int}:R_σ ratio and GoF value. The error in bond lengths, estimated by comparison with a second refinement using a slightly altered data reduction, is approximately ± 0.03 Å. Crystallographic data (excluding structure factors) for the structure of **2** reported in this paper has been deposited with the Cambridge Crystallographic Data center as supplementary publication No. CCDC 615757. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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