

# Three-dimensional supramolecular structures in (*E,E*)-*N,N'*-bis(4-nitrobenzylidene)butane-1,4-diamine and (*E,E*)-*N,N'*-bis(4-nitrobenzylidene)-hexane-1,6-diamine

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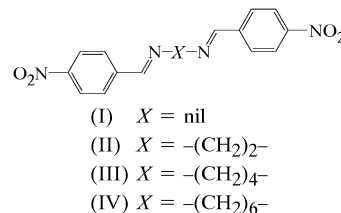
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In both (*E,E*)-*N,N'*-bis(4-nitrobenzylidene)butane-1,4-diamine, C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>, (III), and (*E,E*)-*N,N'*-bis(4-nitrobenzylidene)hexane-1,6-diamine, C<sub>20</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>, (IV), the molecules lie across centres of inversion in space groups *P* $\bar{1}$  and *P*<sub>2</sub><sub>1</sub>/*c*, respectively. In (III), the three-dimensional supramolecular structure is built from  $\pi$ -stacked chains of edge-fused *R*<sub>2</sub><sup>2</sup>(30) rings, while in (IV), chains of edge-fused *R*<sub>2</sub><sup>2</sup>(38) rings are linked by dipolar nitro–nitro interactions.

## Comment

In this paper, we describe the structures of two compounds in the series 4-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH=N–(CH<sub>2</sub>)<sub>*n*</sub>–N=CHC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>, viz. for *n* = 4, compound (III), or *n* = 6, compound (IV) (see scheme). We have recently reported the molecular and supramolecular structures of *N,N'*-bis(4-nitrobenzylidene)-ethane-1,2-diamine, (II), where *n* = 2 (Bomfim *et al.*, 2005). The molecules of (II), which lie across centres of inversion in the space group *P*<sub>2</sub><sub>1</sub>/*n*, are linked into sheets by a single C–H...O hydrogen bond, and these sheets are further linked by an aromatic  $\pi$ – $\pi$  stacking interaction. By contrast, in (*E,E*)-1-(3-nitrophenyl)-4-(4-nitrophenyl)-2,3-diaza-1,3-butadiene, (I), where there are no methylene groups between the two –CH=N– units, the centrosymmetric molecules are linked directly into a three-dimensional framework structure by means of two independent C–H...O hydrogen bonds (Glidewell *et al.*, 2006). Intrigued by the differences in the aggregation patterns of these two compounds, we have now undertaken a more extended study involving compounds (III) and (IV), and report their structures here.

Compounds (I)–(IV) all lie across centres of inversion and all have the *E,E* configuration at the C=N double bonds. In each of compounds (III) and (IV) (Figs. 1 and 2), the reference molecule was selected, for the sake of convenience, as that centred across ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) in the space groups *P* $\bar{1}$  and *P*<sub>2</sub><sub>1</sub>/*c*, respectively.



In each of compounds (II)–(IV), the nitro groups are essentially coplanar with the adjacent aryl rings, as shown by the relevant torsion angles (Table 1) and, likewise, the C1–C11–N11–C12 fragments are effectively coplanar with these rings. However, the skeletons in the polymethylene spacer units adopt conformations which are very far from planar.

In compound (III) (Fig. 1), the molecules are linked into chains of edge-fused rings, which can alternatively be described as molecular ladders, by a single C–H...O hydrogen bond (Table 2), and these chains are further linked into a three-dimensional framework by two independent  $\pi$ – $\pi$  stacking interactions. The methine C11 atoms at (*x*, *y*, *z*) and

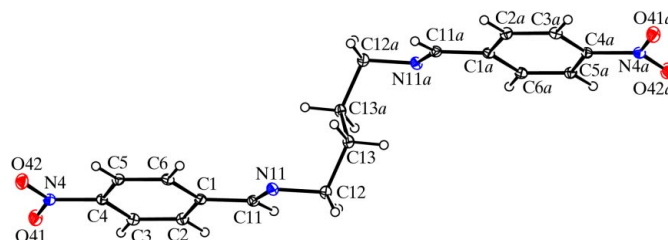


Figure 1

The molecule of compound (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix 'a' are at the symmetry position (1 – *x*, 1 – *y*, 1 – *z*).

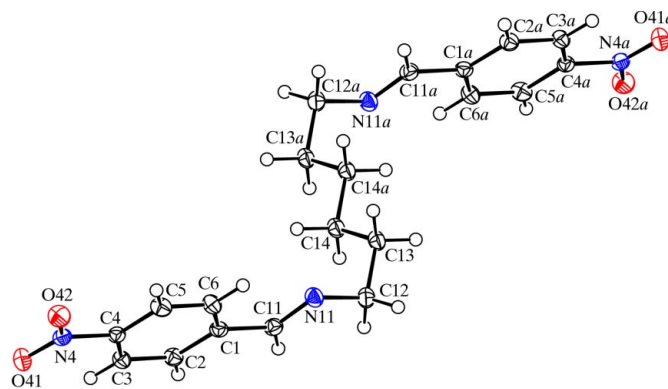
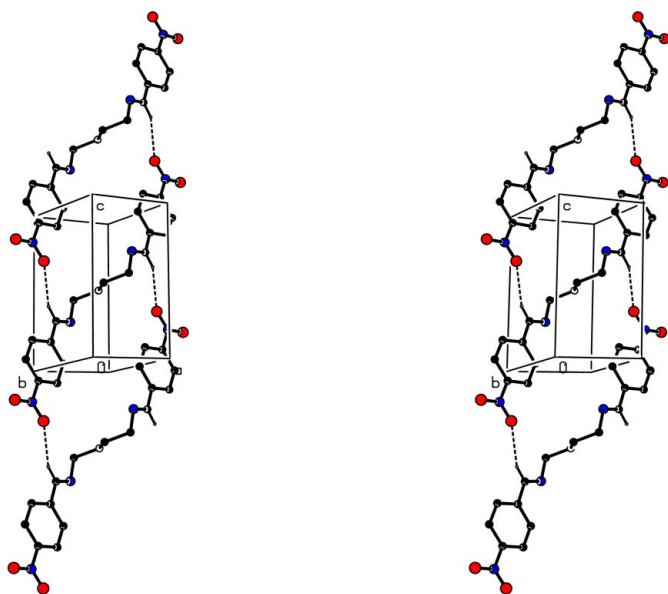


Figure 2

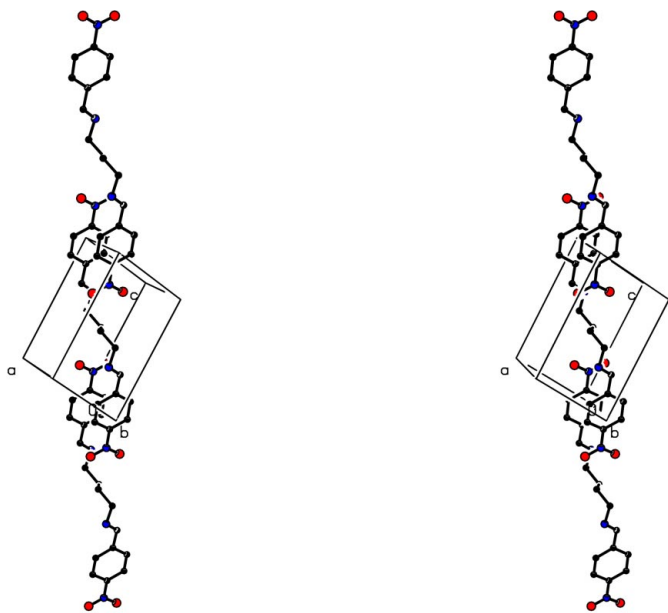
The molecule of compound (IV), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix 'a' are at the symmetry position (1 – *x*, 1 – *y*, 1 – *z*).

$(1-x, 1-y, 1-z)$  are parts of the molecule centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . These atoms act as hydrogen-bond donors to the nitro atoms O42 at  $(x, y, 1+z)$  and  $(1-x, 1-y, -z)$ , respectively, which themselves are parts of the molecules centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$  and  $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ , respectively. Propagation by translation and inversion of this single hydrogen bond then generates a chain of edge-fused  $R_2^2(30)$  rings (Bernstein *et al.*, 1995) running along  $(\frac{1}{2}, \frac{1}{2}, z)$  (Fig. 3).



**Figure 3**

A stereoview of part of the crystal structure of (III), showing the formation of a chain of edge-fused  $R_2^2(30)$  rings along [001]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.



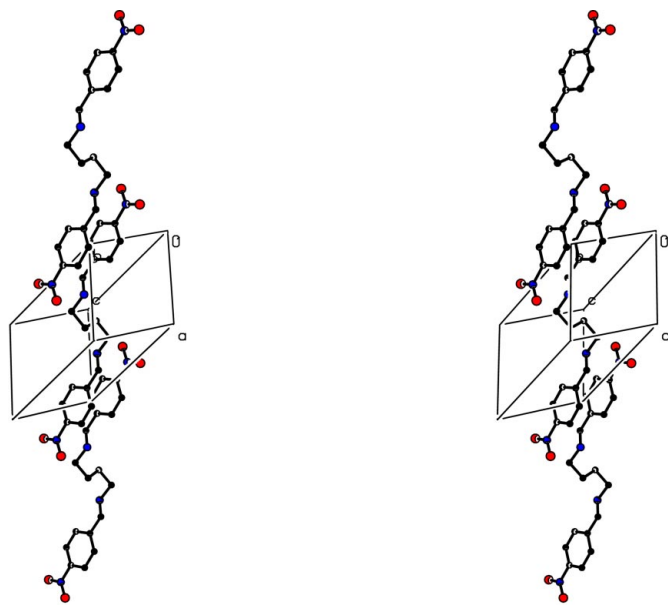
**Figure 4**

A stereoview of part of the crystal structure of (III), showing the formation of a  $\pi$ -stacked chain along [101]. For the sake of clarity, all H atoms have been omitted.

The aryl rings at  $(x, y, z)$  and  $(-x, 1-y, -z)$ , which form parts of molecules centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and  $(-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ , are strictly parallel, with an interplanar spacing of 3.738 (2) Å; the centroid separation is 3.377 (2) Å, corresponding to a ring offset of 1.602 (2) Å. Propagation by inversion of this stacking interaction then generates a chain running parallel to the [101] direction (Fig. 4). Similarly, the rings at  $(x, y, z)$  and  $(-x, 2-y, -z)$  are parallel, with an interplanar spacing of 3.630 (2) Å, and a centroid separation and offset of 3.378 (2) and 1.327 (2) Å, respectively. This stacking interaction generates a chain parallel to the  $[1\bar{1}1]$  direction (Fig. 5). The combination of the [001], [101] and  $[1\bar{1}1]$  chains suffices to link all of the molecules into a single three-dimensional structure.

In compound (IV) (Fig. 2), the molecules are linked by a single C—H...O hydrogen bond (Table 2), but aromatic  $\pi$ — $\pi$  stacking interactions are absent from the structure. Instead, the hydrogen-bonded chains are linked, again into a three-dimensional structure, by a single dipolar nitro—nitro interaction. The aryl C2 atoms at  $(x, y, z)$  and  $(1-x, 1-y, 1-z)$  act as hydrogen-bond donors to nitro atoms O42 at  $(-1+x, -1+y, z)$  and  $(2-x, 2-y, 1-z)$ , which are themselves parts of the molecules centred at  $(-\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$  and  $(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$ , respectively. Propagation of this single hydrogen bond thus generates a chain of edge-fused  $R_2^2(38)$  rings running parallel to the [110] direction (Fig. 6).

Nitro atom O41 at  $(x, y, z)$  forms a short dipolar contact with nitro atom N4 at  $(3-x, \frac{1}{2}+y, \frac{3}{2}-z)$ ; the dimensions of this contact are  $N\cdots O = 2.893$  (2) Å,  $N-O\cdots N = 117.2$  (2)° and  $O\cdots N-C = 118.4$  (2)°; so that it is somewhat reminiscent of the type I (perpendicular) dipolar carbonyl—carbonyl interaction (Allen *et al.*, 1998). In this manner, the molecule centred at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  acts as donor to the molecules centred at

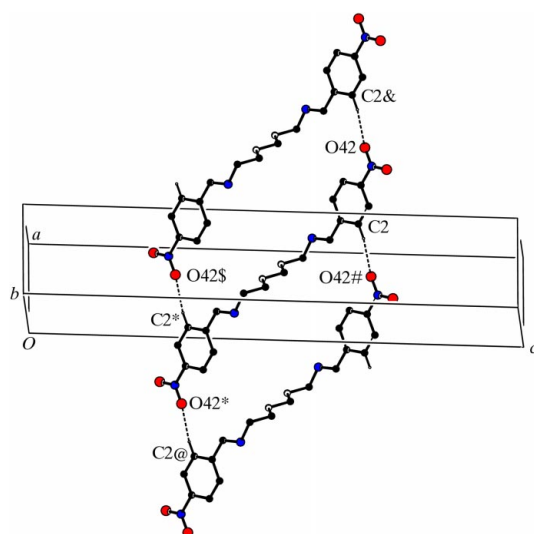


**Figure 5**

A stereoview of part of the crystal structure of (III), showing the formation of a  $\pi$ -stacked chain along  $[1\bar{1}1]$ . For the sake of clarity, all H atoms have been omitted.

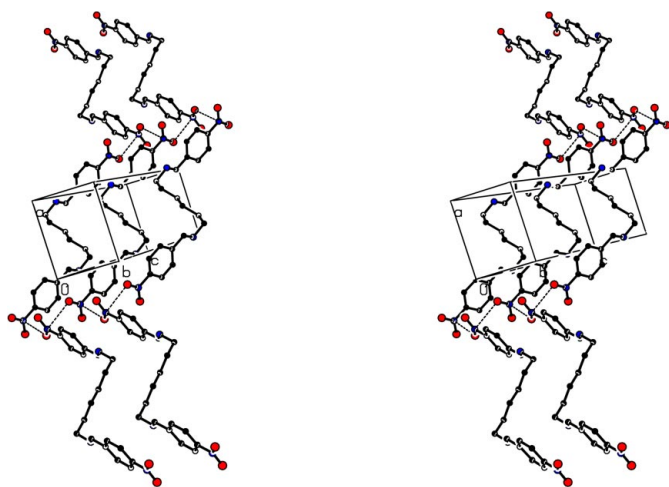
( $\frac{5}{2}, 1, 1$ ), and ( $-\frac{3}{2}, 0, 0$ ) and as acceptor from those centred at ( $\frac{5}{2}, 0, 1$ ) and ( $-\frac{3}{2}, 1, 0$ ), so generating a ( $\bar{1}04$ ) sheet in the form of a (4,4)-net built from a single type of  $R_4^4(46)$  ring (Starbuck *et al.*, 1999) (Fig. 7). The combination of these sheets and the hydrogen-bonded [110] chains links all the molecules into a single three-dimensional framework.

Hence, although compounds (I)–(IV) all form three-dimensional supramolecular structures, no two exhibit the same range of direction-specific intermolecular interactions, and the details of the framework formation are different for each.



**Figure 6**

Part of the crystal structure of (IV), showing the formation of a chain of edge-fused  $R_2^2(38)$  rings along [110]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (\*), hash (#), ampersand (&), dollar sign (\$) or 'at' symbol (@) are at the symmetry positions  $(1-x, 1-y, 1-z)$ ,  $(-1+x, -1+y, z)$ ,  $(1+x, 1+y, z)$ ,  $(2-x, 2-y, 1-z)$  and  $(-x, -y, 1-z)$ , respectively.



**Figure 7**

A stereoview of part of the crystal structure of (IV), showing the formation of a ( $\bar{1}04$ ) sheet of  $R_4^4(46)$  rings generated by the dipolar nitro–nitro interaction. For the sake of clarity, all H atoms have been omitted.

## Experimental

A solution of 4-nitrobenzaldehyde (8 mmol) and 1,4-diaminobutane (4 mmol) in methanol (25 ml) was heated under reflux for 30 min. After cooling, the solvent was removed under reduced pressure and the product was recrystallized from methanol–1,2-dichloroethane (1:1 v/v) to yield crystals of (III) suitable for single-crystal X-ray diffraction (m.p. 438–439 K). Compound (IV) was prepared in a similar way from 4-nitrobenzaldehyde and 1,6-diaminohexane, but it was recrystallized from 1,2-dichloroethane (m.p. 408–410 K).

## Compound (III)

### Crystal data

$C_{18}H_{18}N_4O_4$   
 $M_r = 354.36$   
 Triclinic,  $P\bar{1}$   
 $a = 7.1162$  (4) Å  
 $b = 7.1895$  (2) Å  
 $c = 9.1695$  (4) Å  
 $\alpha = 83.210$  (3)°  
 $\beta = 78.920$  (2)°  
 $\gamma = 64.808$  (3)°  
 $V = 416.25$  (3) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.414$  Mg m<sup>−3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 1895 reflections  
 $\theta = 3.1$ – $27.6$ °  
 $\mu = 0.10$  mm<sup>−1</sup>  
 $T = 120$  (2) K  
 Lath, colourless  
 $0.46 \times 0.34 \times 0.13$  mm

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.944$ ,  $T_{\max} = 0.987$   
 8689 measured reflections

1895 independent reflections  
 1589 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$   
 $\theta_{\max} = 27.6$ °  
 $h = -9 \rightarrow 9$   
 $k = -9 \rightarrow 9$   
 $l = -11 \rightarrow 11$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.114$   
 $S = 1.05$   
 1893 reflections  
 118 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 0.1082P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.26$  e Å<sup>−3</sup>  
 $\Delta\rho_{\min} = -0.34$  e Å<sup>−3</sup>

## Compound (IV)

### Crystal data

$C_{20}H_{22}N_4O_4$   
 $M_r = 382.42$   
 Monoclinic,  $P2_1/c$   
 $a = 6.1908$  (3) Å  
 $b = 4.9761$  (2) Å  
 $c = 30.1095$  (15) Å  
 $\beta = 94.331$  (3)°  
 $V = 924.91$  (7) Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.373$  Mg m<sup>−3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 2083 reflections  
 $\theta = 3.3$ – $27.6$ °  
 $\mu = 0.10$  mm<sup>−1</sup>  
 $T = 120$  (2) K  
 Lath, colourless  
 $0.44 \times 0.30 \times 0.12$  mm

**Table 1**

Selected torsion angles (°) for compounds (II)–(IV).

Parameter	(II) <sup>†</sup>	(III)	(IV)
C3–C4–N4–O41	−5.86 (15)	0.96 (15)	−2.3 (2)
C2–C1–C11–N11	177.91 (9)	−171.77 (10)	172.20 (15)
C1–C11–N11–C12	−176.58 (8)	−179.54 (9)	−179.72 (12)
C11–N11–C12–C12 <sup>i</sup>	118.31 (13)		
C11–N11–C12–C13		111.42 (11)	111.90 (15)
N11–C12–C13–C13 <sup>i</sup>		−65.67 (15)	
N11–C12–C13–C14			−70.53 (15)
C12–C13–C14–C14 <sup>i</sup>			−179.76 (15)

Symmetry code: (i)  $1-x, 1-y, 1-z$ . <sup>†</sup> Data for compound (II) from Bomfim *et al.* (2005).

### Data collection

Nonius KappaCCD area-detector diffractometer	2083 independent reflections
$\varphi$ and $\omega$ scans	1516 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.041$
$T_{\text{min}} = 0.952$ , $T_{\text{max}} = 0.988$	$\theta_{\text{max}} = 27.6^\circ$
7409 measured reflections	$h = -8 \rightarrow 7$
	$k = -6 \rightarrow 6$
	$l = -31 \rightarrow 39$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.2054P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.19 \text{ e } \text{\AA}^{-3}$
2083 reflections	$\Delta\rho_{\text{min}} = -0.30 \text{ e } \text{\AA}^{-3}$
127 parameters	
H-atom parameters constrained	

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for compounds (III) and (IV).

Compound	$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
(III)	$C11-H11 \cdots O42^i$	0.95	2.60	3.502 (2)	159
(IV)	$C2-H2 \cdots O42^{ii}$	0.95	2.50	3.349 (2)	149

Symmetry codes: (i)  $x, y, 1+z$ ; (ii)  $-1+x, -1+y, z$ .

Crystals of compound (III) are triclinic. The space group  $P\bar{1}$  was selected and confirmed by the subsequent structure analysis. For compound (IV), the space group  $P2_1/c$  was uniquely determined from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 or 0.99  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s)

used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton; the authors thank the staff for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1882). Services for accessing these data are described at the back of the journal.

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