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Acta Cryst. (1993). C**49**, 278–282

Structure and Conformation of 3-(Dibenzylamino)phenylacetonitrile

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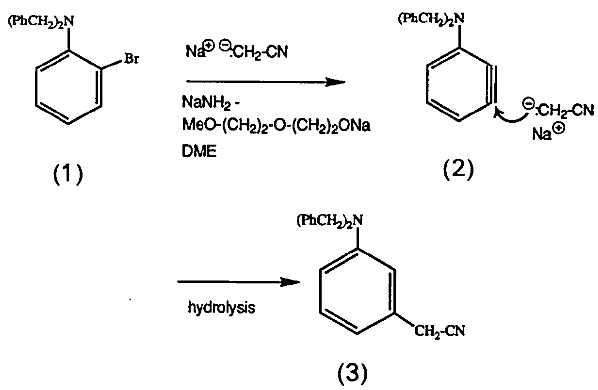
(*Received* 29 *January* 1992; *accepted* 20 *July* 1992)

Abstract. $C_{22}H_{20}N_2$, $M_r = 312.41$, orthorhombic, $P2_12_12_1$, $Z = 4$, $F(000) = 664$. For Mo $K\alpha_1$, $\lambda = 0.070930$ Å, $a = 6.021$ (1), $b = 15.989$ (4), $c = 17.906$ (5) Å, $V = 1723.8$ (7) Å^3, $D_x = 1.204$ Mg m^{-3}, $\mu = 0.0659$ mm^{-1} for 1774 measured reflections. For Cu $K\alpha_1$, $\lambda = 1.540562$ Å, $a = 6.025$ (1), $b = 15.990$ (5), $c = 17.921$ (2) Å, $V = 1726.5$ (6) Å^3, $D_x = 1.202$ Mg m^{-3}, $\mu = 0.5088$ mm^{-1} for 1942 measured reflections. The crystal structure analysis of the title compound confirms the prevailing *meta*-directing effect of nitrogen in arynic condensation reactions. The results of two analyses, carried out on data collected with Mo $K\alpha$ and Cu $K\alpha$ radiations, are in quite good agreement showing that, when the crystal sample is good, acceptable results can be obtained even with an unfavourable ratio between the number of observations and the number of refined parameters.

Introduction. As part of our study on the arynic condensation of nitrile enolates, in order to obtain starting materials for further synthesis, the condensation reaction below has been carried out (DME = 1,2-dimethoxyethane). Compound (3) is of particular interest since the benzyl groups can be removed to give the corresponding aniline which can be easily functionalized.



Although the prevailing *meta*-directing effect of nitrogen in arynic condensations is well established, some exceptions are known (Pansegrau, Rieker & Meyers, 1988). Moreover, it was not possible to assign the correct structure to compound (3), as even the ^{1}H and ^{13}C NMR data were not enough for this purpose. For these reasons the X-ray crystal structure analysis of this compound was carried out, by collecting the intensity data with molybdenum radiation initially, and then with copper radiation,

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Table 1. *Experimental data for the crystal structure analyses*

	Mo $K\alpha$	Cu $K\alpha$
Diffractometer	Enraf–Nonius CAD-4	Siemens AED
Reflections for lattice parameters		
Number	25	29
θ range (°)	11–18	23–39
Crystal size (mm)	0.28 × 0.33 × 0.39	0.28 × 0.33 × 0.39
Extinction g factor	Not applied	0.89 (5) × 10^{-7}
Scan speed (° min^{-1})	1.6–3.3	3–12
Scan width (°)	0.80 + 0.35tanθ	1.20 + 0.14tanθ
θ range (°)	3–25	3–70
h range	0–7	0–7
k range	0–19	0–19
l range	0–21	0–21
Standard reflection	2,9,9	2,8,10
Intensity variation	None	None
Scan mode	θ–2θ	θ–2θ
Number of measured reflections	1774	1942
Condition for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Number of reflections used in refinement	764	1452
Max. LS shift to e.s.d. ratio	0.390	0.056
Min., max. height in final $\Delta\rho$ (e Å^{-3})	−0.14, 0.07	−0.13, 0.09
Number of refined parameters	297	297
$R = \sum\Delta F/\sum F_o$	0.0257	0.0332
$wR = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$	0.0259	0.0298
$S = [\sum w(\Delta F)^2/(N-P)]^{1/2}$*	0.6665	0.4815
w	Unit	Unit

* P = number of parameters, N = number of observations.

as with the first data set the ratio between the number of observations and the number of refined parameters was rather unfavourable. In the present paper the results of the two analyses are compared and the molecular structure and conformation are discussed.

Experimental. Two series of intensity data were collected with the same sample, initially using Mo $K\alpha$ radiation and then Cu $K\alpha$ radiation, because the Mo data gave a ratio between the number of observations and the number of refined parameters (2.6) which was too low. For the Cu data this ratio improves to 4.9, but remains well below the recommended value (> 10). Table 1 summarizes the relevant data of the crystal structure analyses carried out on both sets of data.

The molecular geometries derived from these data were compared by means of the probability-plot analysis (Abrahams & Keve, 1971) using all interatomic distances not involving H atoms to a limit of 4.65 Å (De Camp, 1973). From the half-normal probability plot of Fig. 1, calculated by the *ABRAHAMS* program (Gilli, 1977), it appears that the two series of data are normally distributed with no significant systematic errors in the case of distances (apart from a small overestimate of the e.s.d.'s), the slope and intercept of the least-squares lines being 0.913 (7) and −0.005 (7) (r = 0.996), respectively (Fig. 1*a*); while for the atomic anisotropic displacements, the slope and intercept are 2.55 (6) and −0.62 (6) (r = 0.959), respectively, indicating that the e.s.d.'s are underestimated (Fig. 1*b*) and the two sets of data are affected by systematic effects, probably in connection with the uncorrected absorption.

Comparison of single goemetrical parameters (bond distances, bond angles, torsion angles *etc.*) from the two sets of data shows that there are no

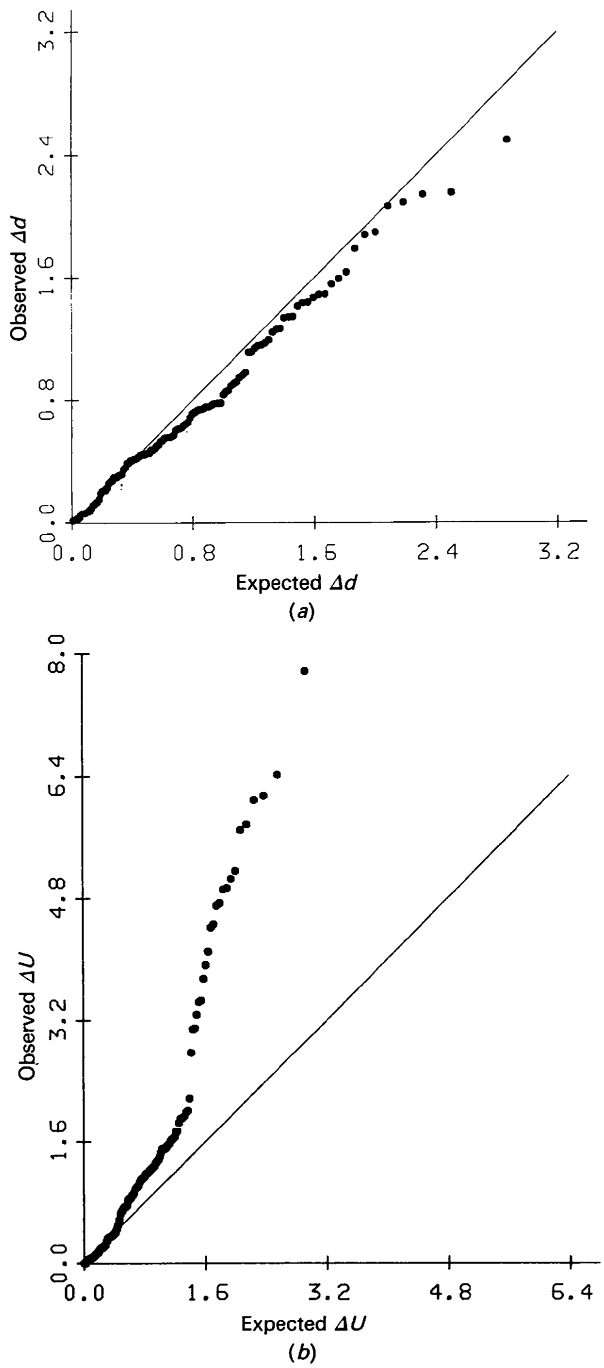


Fig. 1. Half-normal probability plots comparing the results of the analyses carried out with Mo and Cu data: (*a*) comparison of all interatomic distances < 4.65 Å and (*b*) comparison of U_{ij} values.

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic atomic displacement parameters* ($Å^2 \times 10^4$) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
N1	1401 (4)	424 (2)	7164 (1)	544 (8)
N2	4977 (7)	−2809 (2)	9290 (2)	882 (13)
C1	3491 (6)	868 (2)	7214 (2)	553 (11)
C2	3586 (5)	1586 (2)	7764 (2)	487 (9)
C3	5489 (6)	2083 (2)	7779 (2)	592 (11)
C4	5658 (7)	2751 (2)	8272 (2)	725 (14)
C5	3942 (8)	2914 (2)	8755 (2)	765 (15)
C6	2046 (7)	2435 (2)	8745 (2)	699 (13)
C7	1871 (6)	1768 (2)	8246 (2)	564 (11)
C8	−194 (7)	708 (2)	6613 (2)	562 (11)
C9	−447 (5)	150 (2)	5932 (1)	485 (9)
C10	1207 (6)	−412 (2)	5727 (2)	571 (11)
C11	967 (7)	−901 (2)	5092 (2)	682 (13)
C12	−921 (8)	−837 (2)	4662 (2)	722 (14)
C13	−2571 (7)	−281 (3)	4860 (2)	695 (13)
C14	−2341 (6)	211 (2)	5497 (2)	580 (11)
C15	914 (5)	−230 (2)	7647 (2)	476 (9)
C16	−1031 (5)	−702 (2)	7554 (2)	529 (10)
C17	−1492 (6)	−1361 (2)	8034 (2)	615 (12)
C18	−82 (6)	−1565 (2)	8610 (2)	622 (12)
C19	1838 (6)	−1107 (2)	8706 (2)	532 (10)
C20	2339 (6)	−444 (2)	8236 (2)	512 (10)
C21	3385 (8)	−1303 (2)	9347 (2)	654 (13)
C22	4281 (7)	−2152 (2)	9314 (2)	629 (12)

significant differences and the values are quite consistent from the chemical point of view. In the following discussion only data from the Cu *Kα* analysis will be considered.

The integrated intensities were measured using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. Corrections for Lorentz and polarization effects were applied but no corrections were applied for absorption, while extinction was considered according to Zachariasen (1963) for the Cu data only.

The structure was determined by direct methods with *SHELXS*86 (Sheldrick, 1986) and refined by anisotropic full-matrix least squares on *F*, using *SHELX*76 (Sheldrick, 1976). The H atoms were located from a difference Fourier synthesis and refined isotropically. No attempt was made to determine the absolute structure. The atomic scattering factors and the anomalous-scattering coefficients were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final atomic coordinates from the Cu data are given in Table 2.*

The calculations were carried out on the Encore-Gould-Powernode 6040 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma). In addition to the quoted programs, *LQPARM* (Nardelli & Mangia, 1984), *PARST* (Nardelli, 1983), *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1976) have been used.

Discussion. An *ORTEP* drawing of the molecule is displayed in Fig. 2 and in Table 3 the values of bond distances and angles from the two sets of data are compared. The differences between the corresponding values of the two sets of data are never significant, the ratio Δ/σ being less than 1.38 for distances, and 1.89 for angles. The e.s.d.'s of the Mo data are (on average) 1.80 and 1.71 times greater than those of the Cu data for distances and angles respectively. The average value of the bond distances is 1.399 (9) Å for the Mo data and 1.400 (5) Å for the Cu data giving $\Delta/\sigma = 0.11$; the corresponding values for bond angles are 121.3 (5), 121.4 (3)° and 0.18, respectively.

These data show that the results of the analysis with Mo data are quite good in spite of the limited number of reflections, so rejection of a structure analysis solely on the basis of an unfavourable ratio between the number of observations and the number of refined parameters is not always defensible. Within reasonable limits, the goodness of data is certainly more important than their number.

The analysis of the molecular displacements was carried out on the Cu data in terms of the **LST** rigid-body model according to Schomaker & Trueblood (1968) and Trueblood (1978), also considering the internal motions according to Dunitz & White (1973) using the *THMV* program (Trueblood, 1984). The results of this analysis for the two sets of intensity data are summarized in Table 4.

The position of the acetonitrile substituent in the aniline ring is *meta*, which is in agreement with the

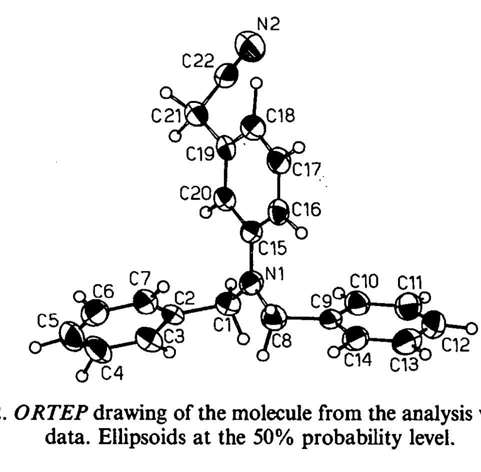


Fig. 2. *ORTEP* drawing of the molecule from the analysis with Cu data. Ellipsoids at the 50% probability level.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55604 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1003]

Table 3. *Comparison of bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *from the two analyses carried out with Mo and Cu data with e.s.d.'s in parentheses*

	Mo data	Cu data		Mo data	Cu data
N1—C1	1.442 (8)	1.448 (4)	C9—C14	1.387 (8)	1.386 (5)
N1—C8	1.457 (8)	1.451 (4)	C10—C11	1.376 (8)	1.389 (5)
N1—C15	1.388 (7)	1.387 (4)	C11—C12	1.374 (11)	1.378 (6)
N2—C22	1.120 (8)	1.132 (5)	C12—C13	1.391 (11)	1.380 (6)
C1—C2	1.527 (8)	1.515 (4)	C13—C14	1.391 (9)	1.393 (5)
C2—C3	1.395 (8)	1.395 (5)	C15—C16	1.400 (8)	1.404 (4)
C2—C7	1.371 (8)	1.378 (5)	C15—C20	1.399 (8)	1.403 (4)
C3—C4	1.394 (9)	1.390 (5)	C16—C17	1.382 (8)	1.389 (5)
C4—C5	1.370 (11)	1.372 (6)	C17—C18	1.384 (9)	1.376 (5)
C5—C6	1.363 (11)	1.375 (6)	C18—C19	1.374 (9)	1.380 (5)
C6—C7	1.391 (9)	1.397 (5)	C19—C20	1.391 (7)	1.388 (4)
C8—C9	1.529 (7)	1.521 (4)	C19—C21	1.514 (9)	1.512 (5)
C9—C10	1.383 (8)	1.390 (5)	C21—C22	1.470 (9)	1.462 (5)
C8—N1—C15	121.4 (5)	121.4 (3)	C10—C11—C12	120.7 (6)	120.2 (3)
C1—N1—C15	120.5 (5)	121.0 (3)	C11—C12—C13	119.4 (6)	119.9 (3)
C1—N1—C8	118.1 (4)	117.6 (3)	C12—C13—C14	120.4 (7)	120.2 (4)
N1—C1—C2	115.3 (5)	116.4 (3)	C9—C14—C13	119.3 (6)	120.2 (3)
C1—C2—C7	122.8 (5)	122.6 (3)	N1—C15—C20	121.3 (5)	121.6 (3)
C1—C2—C3	118.0 (5)	118.4 (3)	N1—C15—C16	120.6 (5)	120.5 (3)
C3—C2—C7	119.3 (5)	118.9 (3)	C16—C15—C20	118.1 (5)	117.9 (3)
C2—C3—C4	120.0 (6)	120.6 (3)	C15—C16—C17	120.4 (5)	120.1 (3)
C3—C4—C5	119.7 (6)	119.5 (4)	C16—C17—C18	121.1 (6)	121.4 (3)
C4—C5—C6	120.6 (6)	120.8 (4)	C17—C18—C19	119.0 (5)	119.1 (3)
C5—C6—C7	120.3 (7)	119.7 (4)	C18—C19—C21	120.0 (5)	120.2 (3)
C2—C7—C6	120.2 (6)	120.4 (3)	C18—C19—C20	120.9 (5)	120.8 (3)
N1—C8—C9	115.4 (5)	115.3 (3)	C20—C19—C21	119.0 (5)	119.0 (3)
C8—C9—C14	118.7 (5)	119.5 (3)	C15—C20—C19	120.5 (5)	120.7 (3)
C8—C9—C10	121.3 (5)	121.3 (3)	C19—C21—C22	113.3 (5)	112.9 (3)
C10—C9—C14	120.0 (5)	119.2 (3)	N2—C22—C21	179.1 (6)	179.9 (4)
C9—C10—C11	120.2 (6)	120.3 (3)			
C8—N1—C15—C16	6.9 (8)	7.9 (4)	N1—C1—C2—C7	6.7 (8)	6.1 (4)
C1—N1—C15—C20	6.5 (8)	5.1 (4)	N1—C8—C9—C10	−21.8 (8)	−21.2 (4)
C15—N1—C1—C2	−87.4 (6)	−85.9 (4)	C18—C19—C21—C22	60.3 (8)	61.2 (4)
C15—N1—C8—C9	−75.2 (6)	−76.0 (4)			

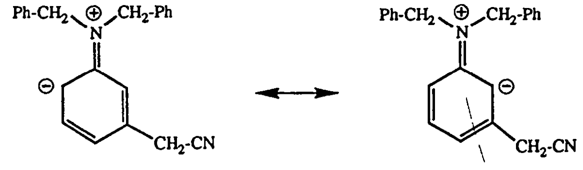
Table 4. *Analysis of the atomic anisotropic displacement in terms of* **LST** *rigid-body motion and internal motions*

	Treatment	$\Delta \times 10^4$ (Å)	$\sigma(w\Delta U) \times 10^4$ (Å^2)	$\sigma(U_o) \times 10^4$ (Å^2)	wR_U
Mo data	Rigid body	87 (114)	68	37	0.194
	Internal motions		50		0.141
Cu data	Rigid body	63 (85)	56	20	0.141
	Internal motions		38		0.097

Group librating	Libration along	Libration amplitude Mo data	Cu data
C22, N2	C19—C21	3.2 (16)	4.1 (10)
C3–C7	C2—PF1	4.9 (5)	4.8 (4)
C10–C14	C9—PF2	4.8 (5)	4.6 (4)
C16–C20	C15—PF3	2.6 (6)	1.9 (6)
N1, C1, C8	C15—PF3	2.3 (8)	2.7 (5)

PF1 = point on the normal at C2 to the mean plane through the C2–C7 phenyl; PF2 = point on the normal at C9 to the mean plane through the C9–C14 phenyl; PF3 = point on the normal at C15 to the mean plane through the C15–C20 phenyl; Δ = mean difference of the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms; $\Delta U = U_{ij}(\text{obs}) - U_{ij}(\text{calc.})$; $wR_U = [\Sigma(w\Delta U)^2/\Sigma(wU_o)^2]^{1/2}$; $\sigma(w\Delta U) = [\Sigma(w\Delta U)^2/\Sigma w^2]^{1/2}$; $\sigma(U_o)$ = mean e.s.d. of U_o values.

directing effect commonly exerted by nitrogen in arynic condensation reactions. Considering the other structural aspects of the molecule, it is noteworthy that the amine N atom is only 0.018 (2) Å out of the plane of the C atoms it is bonded to, and this plane is nearly coplanar with the aniline ring [dihedral angle 173.5 (1)°]. This, coupled with the values of the N—C(ar.) and C(ar.)—C(ar.) distances in the aniline ring, supports the valence-bond description of this system in terms of the contributions of the following resonance structures which prevent rotation about the N—C(ar.) bond.



The two phenyl rings of the benzyl groups are approximately perpendicular to the plane of the amino group, the dihedral angles they form with it

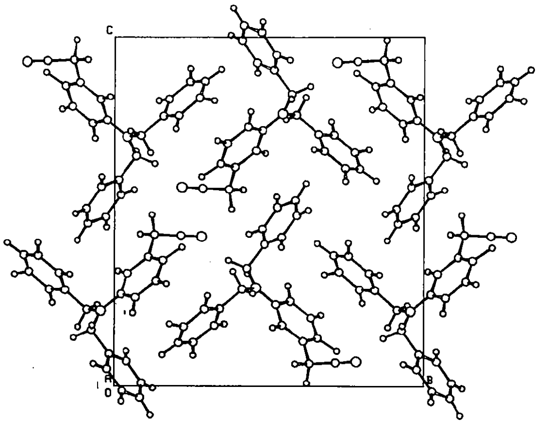


Fig. 3. Packing of the molecules in the unit cell.

being 95.7 (1) and 85.5 (1)° for the C2–C7 and C9–C14 phenyl rings, respectively. No particular trend is observed for the C—C distances in these two rings, while the endocyclic angles at the *ipso* and *meta* C atoms decrease by approximately the same magnitude as those at the *ortho* and *para* C atoms increase. These angular deformations are due to the effect exerted by the amino substitutent, which is in agreement with the findings of Domenicano, Vaciago & Coulson (1975).

The acetonitrile group is linear [CH_2—C≡N = 179.8 (4)°] and is tilted with respect to the benzene plane by 59.1 (1)°, no electronic effect being present to impose any particular orientation. Fig. 3 shows how the molecules are packed in the unit cell under van der Waals interactions.

The authors gratefully acknowledge financial support from the European Economic Community under contract No. SC1000657.

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Acta Cryst. (1993). C**49**, 282–285

Structure of Amprolium Hydrochloride

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(*Received* 21 *January* 1992; *accepted* 23 *June* 1992)

Abstract. 1-[(4-Amino-2-propyl-5-pyrimidinyl)-methyl]-2-methylpyridinium chloride hydrochloride, $C_{14}H_{19}N_4^+.Cl^-.HCl$, $M_r = 315.2$, triclinic, $P\bar{1}$, $a = 11.327$ (2), $b = 13.842$ (2), $c = 10.959$ (2) Å, $\alpha = 90.68$ (2), $\beta = 110.13$ (1), $\gamma = 99.10$ (2)°, $V = 1588.9$ (4) Å^3, $Z = 4$, $D_x = 1.318$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 35.7$ cm^{-1}, $F(000) = 664$, $T = 297$ K, $R = 0.054$ for 3680 reflections with $F \geq 6\sigma(F)$. The two independent divalent amprolium molecular ions are interconnected by four N(4′α)—H···Cl^- (amino group) hydrogen bonds forming a dimeric unit which has a pseudo center of symmetry, discounting the propyl side chains. There are only van der Waals interactions between these dimeric units.

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0108-2701/93/020282-04$06.00