

La Fig. 2 montre que les molécules sont situées au voisinage des plans $y = 0$ et $y = \frac{1}{2}$. Il n'y a pas de liaisons hydrogène intermoléculaires. La cohésion de la structure est due uniquement aux forces de van der Waals.

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The Structures of Three N^1, N^1 -Dimethyl- N^2 - p -nitrophenylamidines: Form-, Acet- and 2,2-Dimethylpropanamide

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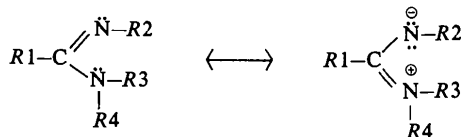
Abstract. N^1, N^1 -Dimethyl- N^2 - p -nitrophenylformamide, (I), $C_9H_{11}N_3O_2$, $M_r = 193.2$, triclinic, $P\bar{1}$, $a = 10.115$ (2), $b = 10.862$ (1), $c = 9.004$ (1) Å, $\alpha = 99.56$ (1), $\beta = 99.25$ (1), $\gamma = 88.83$ (1)°, $V = 962.8$ (2) Å³, $Z = 4$, $D_m = 1.31$, $D_x = 1.33$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 1.54178$ Å, $\mu(\text{Cu } K\alpha) = 7.17$ cm⁻¹, $F(000) = 408$, room temperature, $R = 0.049$ for 1980 observed reflexions. N^1, N^1 -Dimethyl- N^2 - p -nitrophenylacetamide, (II), $C_{10}H_{13}N_3O_2$, $M_r = 207.2$, triclinic, $P\bar{1}$, $a = 10.523$ (3), $b = 12.410$ (3), $c = 9.594$ (3) Å, $\alpha = 96.59$ (2), $\beta = 110.21$ (2), $\gamma = 68.38$ (2)°, $V = 1092.9$ (5) Å³, $Z = 4$, $D_m = 1.27$, $D_x = 1.26$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.55$ cm⁻¹, $F(000) = 440$, room temperature, $R = 0.054$ for 1872 observed reflexions. N^1, N^1 -Dimethyl- N^2 - p -nitrophenyl-2,2-dimethylpropanamide, (III), $C_{13}H_{19}N_3O_2$, $M_r =$

249.3, monoclinic, $P2_1/c$, $a = 10.084$ (4), $b = 7.551$ (3), $c = 19.234$ (5) Å, $\beta = 111.89$ (3)°, $V = 1359.0$ (9) Å³, $Z = 4$, $D_m = 1.21$, $D_x = 1.22$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.49$ cm⁻¹, $F(000) = 536$, room temperature, $R = 0.041$ for 1391 observed reflexions. The amidine N¹–C and C–N² bonds are different in all presented structures. N¹ and the p -nitrophenyl substituent at the C=N² double bond are in *trans* configuration in (I) and (II) and in *cis* configuration in (III). The bond angle N¹–C–N² in (II) (A and B) is 118.7 (3) and 118.2 (3)° (typical of *trans* amidines), in (I) (A and B) it is 123.6 (3) and 123.2 (3)° (owing to the small substituent at C_{amidine}), and it is 124.2 (2)° in (III) as a result of the *cis* configuration.

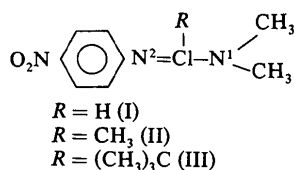
Introduction. This work is part of a series of structural studies on amidine systems carried out in this

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laboratory* which aim at tracing the changes induced in the geometry of the amidine group by different substituents and at determining factors governing the *cis-trans* (C=N² bond) isomerism of the amidine system. The amidine group, like the amide group, tends to be planar owing to the partial double-bond character of the C–N¹ bond, as indicated by the mesomeric forms below.



Planarity of the substituted amidine core ensures optimal interaction between trigonally hybridized C and N atoms at the energy cost required to bring the bonds at the N atom into the common plane. Bulky substituents at the amidine core introduce steric hindrance and, depending on the size of the substituent, can force the molecule to undergo some geometrical and conformational changes to relieve the strain or, as found in the extreme case of *N*¹,*N*¹-(2,6-dimethylpentamethylene)-*N*²-phenyl-2,2-dimethylpropanamidine (Gilli & Bertolasi, 1979), can produce a total decoupling between the amidine π electrons and the $2p$ orbital of the imine N atom. In the present work we have concentrated our attention on the effect of the substituent at the amidine C atom. This paper reports the crystal structures of three *N*¹,*N*¹-dimethyl-*N*²-*p*-nitrophenylamidines with H (I), CH₃ (II) and (CH₃)₃C (III) substituents at the amidine C atom.



Experimental. Title compounds were synthesized by Oszczapowicz & Raczynska (1983, 1984) [(I) and (II)], and Oszczapowicz & Ciszkowski (1987) [(III)]. Yellow prismatic crystals obtained from absolute ethanol; density by flotation. Crystals of (I) and (III) decomposed in the air and were therefore mounted in glass capillaries. Lattice symmetries from Weissenberg photographs. Syntex P2₁ diffractometer, graphite monochromator, θ - 2θ scan technique. Unit-cell parameters from least-squares fitting of 15 counter reflexions. Experimental details are in Table 1.

Peak profile analysis according to Lehmann & Larsen (1974); Lorentz and polarization factors; no

* Previous paper: Surma, Jaskólski, Kosturkiewicz & Oszczapowicz (1988).

Table 1. *Experimental details*

	(I)	(II)	(III)
Crystal size (mm)	0.3 × 0.3 × 0.4	0.4 × 0.5 × 0.5	0.5 × 0.7 × 0.8
Wavelength (Å)	1.54178	0.71069	0.71069
2 θ range of reflexions for cell determination (°)	17–30	13–21	12–23
Max. 2 θ in intensity measurements (°)	115	45	48
Range of <i>h</i>	–10 to 10	–11 to 10	–11 to 10
<i>k</i>	–11 to 11	–13 to 13	0 to 8
<i>l</i>	0 to 9	0 to 13	0 to 22
Standard reflexions (recorded every 100 reflexions)	211, 020	261, 013	422, 422
Intensity variation (%)	±2.7	±3.7	±3.5
No. of unique reflexions	2528	2666	2033
No. of data with $I \geq 2(\sigma)I$	1980	1872	1391
Empirical isotropic extinction parameter	130 (7) × 10 ^{–8}	190 (1) × 10 ^{–8}	6 (1) × 10 ^{–7}
Weighting scheme	$\sigma^{-2}(F)$	$[\sigma^2(F) + 0.00052F^2]^{-1}$	$\sigma^{-2}(F)$
Final <i>R</i> (<i>wR</i>)	0.049 (0.051)	0.054 (0.076)	0.041 (0.048)
<i>S</i>	5.0	2.6	2.1
Max. Δ/σ	0.04	0.1	0.2
($\Delta\rho$) _{max} (e Å ^{–3})	0.19	0.20	0.15
($\Delta\rho$) _{min} (e Å ^{–3})	–0.15	–0.22	–0.15

absorption correction. Structures solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lesinger, Germain, Declercq & Woolfson, 1980). In (I) and (III) all H atoms and in (II) phenyl H atoms from $\Delta\rho$ maps. Remaining H atoms calculated from methyl-group geometry and optimized with fixed U_{iso} (0.08 Å²). Full-matrix least-squares refinement [function minimized $\sum w(F_o - F_c)^2$] of anisotropic non-H atoms and isotropic H atoms found in $\Delta\rho$ maps. F_c values multiplied by $(1 - xF_c^2/\sin 2\theta)$ where x is empirical isotropic extinction parameter. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Computer programs: *MULTAN80* (Main *et al.*, 1980), *SHELX76* (Sheldrick, 1976) and local programs (Jaskólski, 1982). Molecular illustrations drawn using *ORTEP* (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

Discussion. Atomic parameters are given in Table 2, bond lengths, angles and torsion angles in Table 3.*

ORTEP drawings of the molecules with atom-labelling systems are presented in Fig. 1. Two of the crystals investigated [(I) and (II)] have two independent molecules in the asymmetric units. The C(1)–N(1) and C(1)–N(2) bonds are significantly different in all molecules. Table 3 indicates, however, that there is no uniform pattern of the C(1)–N(1)/C(1)–N(2) bond distances as the C(1)–N(2) bond is fairly similar in all five molecules [average = 1.299 (2) Å] whereas the C(1)–N(1) bond shows an appreciable scatter [1.331 (4)–1.380 (3) Å]. On the other hand, there is a very good agreement between the corresponding

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51432 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2) of (a) (I), (b) (II) and (c) (III)*

$$U_{eq} = \frac{1}{3} \sum_i \sum_k U_{ik} a_i^* a_k^* (\mathbf{a}_i \cdot \mathbf{a}_k).$$

	x	y	z	U_{eq}
(a)				
C(1A)	0.2606 (3)	0.5581 (3)	0.0401 (3)	0.056 (1)
C(2A)	0.4368 (3)	0.6184 (3)	0.2318 (3)	0.048 (1)
C(3A)	0.4784 (3)	0.7093 (3)	0.3592 (4)	0.060 (1)
C(4A)	0.5820 (3)	0.6874 (3)	0.4707 (4)	0.062 (1)
C(5A)	0.6469 (3)	0.5754 (3)	0.4556 (3)	0.053 (1)
C(6A)	0.6110 (3)	0.4843 (3)	0.3298 (4)	0.060 (1)
C(7A)	0.5074 (3)	0.5064 (3)	0.2192 (4)	0.057 (1)
C(8A)	0.0866 (5)	0.4677 (5)	-0.1636 (5)	0.087 (2)
C(9A)	0.1226 (5)	0.6975 (5)	-0.1010 (6)	0.086 (2)
N(1A)	0.1595 (2)	0.5745 (2)	-0.0693 (3)	0.062 (1)
N(2A)	0.3312 (2)	0.6484 (2)	0.1250 (3)	0.056 (1)
N(3A)	0.7564 (3)	0.5509 (3)	0.5731 (3)	0.073 (1)
O(1A)	0.8241 (3)	0.4569 (3)	0.5487 (3)	0.113 (1)
O(2A)	0.7767 (2)	0.6266 (2)	0.6922 (3)	0.092 (1)
C(1B)	0.1263 (3)	0.1397 (3)	-0.2871 (4)	0.059 (1)
C(2B)	0.2334 (3)	0.1195 (3)	-0.0470 (3)	0.054 (1)
C(3B)	0.2291 (3)	0.0525 (3)	0.0717 (3)	0.061 (1)
C(4B)	0.3410 (3)	0.0414 (3)	0.1780 (4)	0.060 (1)
C(5B)	0.4590 (3)	0.1000 (3)	0.1681 (3)	0.050 (1)
C(6B)	0.4653 (3)	0.1698 (3)	0.0550 (3)	0.055 (1)
C(7B)	0.3536 (3)	0.1799 (3)	-0.0503 (3)	0.058 (1)
C(8B)	0.0384 (4)	0.1763 (4)	-0.5435 (4)	0.083 (2)
C(9B)	-0.1120 (4)	0.1694 (6)	-0.3524 (6)	0.086 (2)
N(1B)	0.0216 (2)	0.1573 (2)	-0.3915 (3)	0.064 (1)
N(2B)	0.1156 (2)	0.1263 (2)	-0.1499 (3)	0.061 (1)
N(3B)	0.5778 (3)	0.0879 (2)	0.2793 (3)	0.061 (1)
O(1B)	0.6782 (2)	0.1478 (2)	0.2771 (3)	0.086 (1)
O(2B)	0.5734 (2)	0.0174 (2)	0.3724 (2)	0.081 (1)
(b)				
C(1A)	0.9070 (4)	-0.3882 (3)	0.2982 (4)	0.071 (3)
C(2A)	0.8239 (4)	-0.1873 (3)	0.3409 (4)	0.063 (3)
C(3A)	0.8111 (4)	-0.1348 (3)	0.2133 (4)	0.072 (3)
C(4A)	0.8052 (4)	-0.0215 (3)	0.2153 (4)	0.072 (3)
C(5A)	0.8097 (4)	0.0404 (3)	0.3441 (4)	0.065 (2)
C(6A)	0.8222 (4)	-0.0095 (3)	0.4718 (4)	0.070 (2)
C(7A)	0.8281 (4)	-0.1220 (3)	0.4684 (4)	0.067 (2)
C(8A)	0.9790 (5)	-0.5977 (3)	0.2445 (6)	0.111 (4)
C(9A)	0.7558 (6)	-0.4928 (4)	0.3050 (7)	0.129 (4)
C(10A)	1.0401 (5)	-0.3892 (4)	0.2713 (6)	0.106 (3)
N(1A)	0.8828 (4)	-0.4888 (2)	0.2823 (4)	0.084 (2)
N(2A)	0.8187 (3)	-0.2979 (2)	0.3407 (3)	0.073 (2)
N(3A)	0.8028 (4)	0.1592 (3)	0.3450 (5)	0.091 (2)
O(1A)	0.7973 (3)	0.2159 (2)	0.4584 (4)	0.112 (2)
O(2A)	0.8046 (5)	0.1986 (3)	0.2350 (4)	0.149 (3)
C(1B)	0.3733 (4)	0.2435 (3)	0.2752 (4)	0.068 (2)
C(2B)	0.3036 (4)	0.0840 (3)	0.1767 (4)	0.065 (3)
C(3B)	0.1743 (5)	0.0659 (4)	0.1517 (4)	0.071 (3)
C(4B)	0.1707 (5)	-0.0440 (4)	0.1436 (4)	0.073 (3)
C(5B)	0.2952 (4)	-0.1378 (3)	0.1576 (4)	0.072 (3)
C(6B)	0.4253 (5)	-0.1241 (4)	0.1839 (5)	0.089 (3)
C(7B)	0.4285 (5)	-0.0135 (3)	0.1926 (5)	0.084 (3)
C(8B)	0.4497 (5)	0.4133 (4)	0.3586 (5)	0.103 (3)
C(9B)	0.3269 (7)	0.3866 (4)	0.0947 (5)	0.128 (4)
C(10B)	0.4422 (4)	0.1997 (4)	0.4334 (4)	0.085 (3)
N(1B)	0.3808 (4)	0.3449 (3)	0.2468 (4)	0.093 (3)
N(2B)	0.3025 (4)	0.1945 (2)	0.1682 (3)	0.080 (3)
N(3B)	0.2904 (5)	-0.2543 (4)	0.1437 (4)	0.112 (3)
O(1B)	0.4006 (5)	-0.3358 (3)	0.1648 (7)	0.222 (4)
O(2B)	0.1735 (4)	-0.2656 (3)	0.1062 (4)	0.145 (3)
(c)				
N(1)	-0.2180 (2)	0.5275 (3)	0.7024 (1)	0.064 (1)
N(2)	-0.1602 (2)	0.6664 (2)	0.6073 (1)	0.061 (1)
N(3)	0.2340 (3)	0.1677 (3)	0.5842 (1)	0.072 (1)
O(1)	0.3557 (2)	0.2191 (3)	0.5957 (1)	0.102 (1)
O(2)	0.1981 (2)	0.0124 (3)	0.5712 (1)	0.103 (1)
C(1)	-0.2422 (2)	0.6476 (3)	0.6449 (1)	0.055 (1)
C(2)	-0.0646 (2)	0.5386 (3)	0.6024 (1)	0.053 (1)
C(3)	0.0711 (3)	0.5916 (3)	0.6078 (1)	0.061 (1)
C(4)	0.1681 (3)	0.4714 (4)	0.6016 (1)	0.064 (2)
C(5)	0.1292 (2)	0.2956 (3)	0.5879 (1)	0.056 (1)
C(6)	-0.0069 (3)	0.2400 (4)	0.5775 (1)	0.060 (2)
C(7)	-0.1035 (3)	0.3605 (3)	0.5846 (1)	0.059 (1)
C(8)	-0.3301 (5)	0.4318 (5)	0.7174 (3)	0.097 (2)
C(9)	-0.0758 (3)	0.4634 (4)	0.7458 (2)	0.074 (2)
C(10)	-0.3670 (2)	0.7791 (3)	0.6269 (1)	0.061 (1)
C(11)	-0.4988 (3)	0.7037 (5)	0.5642 (2)	0.088 (2)
C(12)	-0.3995 (5)	0.8306 (6)	0.6960 (2)	0.103 (2)
C(13)	-0.3254 (4)	0.9500 (4)	0.5966 (2)	0.079 (2)

C(1)—N bonds within each pair of independent molecules [(I)A, (I)B and (II)A, (II)B]. From the semi-empirical correlation of Norrestam, Mertz & Crossland (1983) ($r = r_o - 0.18p$) between π -bond orders (p) and bond distances (r), where r_o is a standard single-bond distance (1.458 \AA for C—N), the following π -bond orders can be calculated for the present structures: 0.7 in (I), 0.6 in (II) and 0.4 in (III) for the C(1)—N(1)

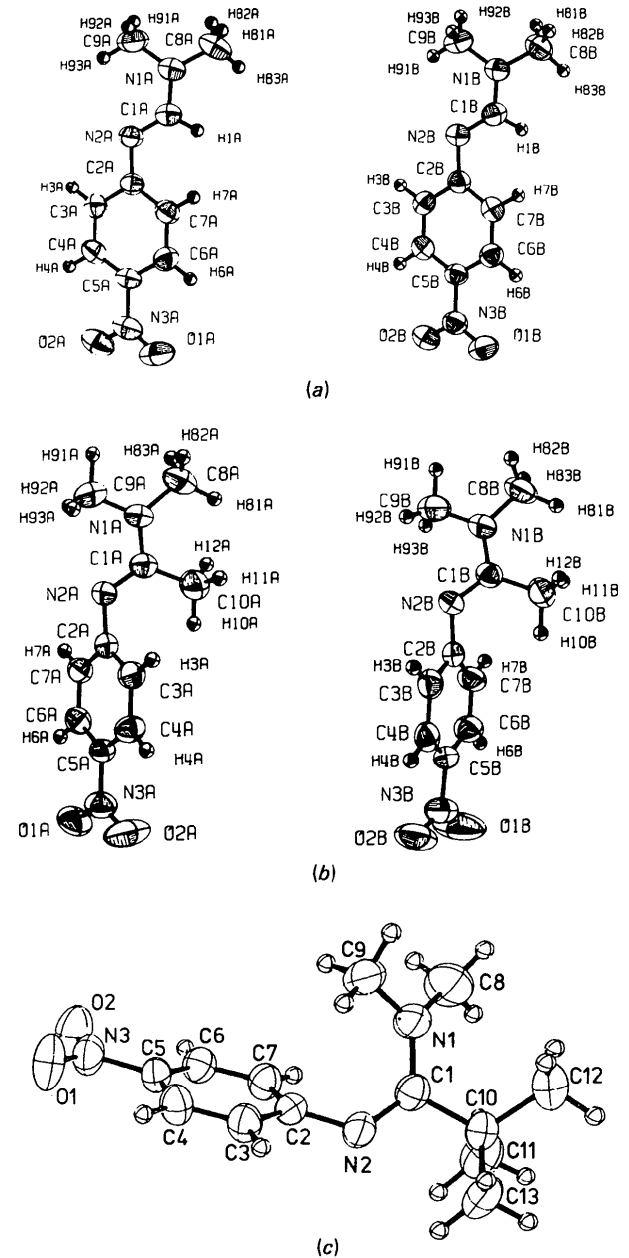


Fig. 1. ORTEP drawings (Johnson, 1976) with the thermal ellipsoids scaled at the 50% probability level and with numbering schemes. H atoms are represented by circles of radius 0.1 \AA . (a) Molecules A and B of (I). (b) Molecules A and B of (II). (c) Molecule of (III).

Table 3. Bond lengths (Å), angles (°) and selected torsion angles (°) with e.s.d.'s in parentheses

	(I)A	(I)B	(II)A	(II)B	(III)
C(1)—N(1)	1.332 (4)	1.331 (4)	1.346 (5)	1.354 (6)	1.380 (3)
C(1)—N(2)	1.289 (4)	1.289 (4)	1.294 (5)	1.281 (5)	1.293 (3)
C(2)—N(2)	1.390 (4)	1.395 (4)	1.393 (5)	1.379 (5)	1.392 (3)
C(2)—C(3)	1.397 (4)	1.396 (4)	1.394 (6)	1.395 (6)	1.392 (3)
C(3)—C(4)	1.376 (5)	1.377 (5)	1.382 (6)	1.371 (7)	1.372 (4)
C(4)—C(5)	1.368 (5)	1.387 (4)	1.374 (6)	1.370 (6)	1.382 (4)
C(5)—C(6)	1.380 (5)	1.376 (4)	1.380 (6)	1.376 (6)	1.376 (3)
C(6)—C(7)	1.371 (4)	1.368 (4)	1.371 (6)	1.377 (7)	1.377 (4)
C(7)—C(2)	1.395 (4)	1.401 (4)	1.385 (6)	1.396 (6)	1.407 (3)
C(5)—N(3)	1.457 (4)	1.454 (4)	1.448 (5)	1.454 (6)	1.453 (3)
N(3)—O(1)	1.227 (4)	1.223 (4)	1.233 (6)	1.195 (7)	1.226 (3)
N(3)—O(2)	1.230 (4)	1.231 (4)	1.222 (6)	1.214 (6)	1.225 (3)
N(1)—C(8)	1.455 (6)	1.454 (5)	1.455 (6)	1.451 (6)	1.458 (5)
N(1)—C(9)	1.441 (6)	1.448 (5)	1.445 (7)	1.451 (7)	1.447 (4)
C(1)—C(10)	—	—	1.504 (6)	1.504 (6)	1.538 (3)
C(10)—C(11)	—	—	—	—	1.532 (4)
C(10)—C(12)	—	—	—	—	1.533 (6)
C(10)—C(13)	—	—	—	—	1.538 (4)
N(1)—C(1)—N(2)	123.6 (3)	123.2 (3)	118.7 (3)	118.2 (3)	124.2 (2)
C(1)—N(2)—C(2)	117.9 (2)	117.9 (2)	122.5 (3)	123.9 (3)	124.4 (2)
N(2)—C(2)—C(3)	117.3 (2)	117.6 (2)	122.6 (3)	120.1 (3)	118.8 (2)
C(3)—C(2)—C(7)	117.5 (3)	117.8 (3)	118.0 (3)	117.7 (4)	118.0 (2)
C(2)—C(3)—C(4)	121.2 (3)	121.2 (3)	120.8 (4)	120.9 (4)	121.1 (3)
C(3)—C(4)—C(5)	119.5 (3)	119.1 (3)	119.4 (4)	119.8 (4)	119.4 (3)
C(4)—C(5)—C(6)	121.1 (3)	121.1 (2)	120.9 (4)	121.2 (4)	121.2 (3)
C(5)—C(6)—C(7)	119.2 (3)	119.3 (3)	119.1 (4)	118.8 (4)	119.2 (3)
C(6)—C(7)—C(2)	121.5 (3)	121.6 (3)	121.8 (4)	121.5 (4)	120.8 (3)
C(7)—C(2)—N(2)	125.1 (2)	124.6 (2)	119.2 (3)	121.8 (3)	122.8 (2)
C(4)—C(5)—N(3)	120.0 (2)	119.4 (2)	119.1 (3)	119.8 (4)	119.2 (2)
C(6)—C(5)—N(3)	118.9 (2)	119.5 (2)	120.0 (3)	119.0 (4)	119.6 (2)
C(5)—N(3)—O(1)	118.9 (3)	118.9 (2)	118.2 (3)	119.4 (4)	118.6 (2)
C(5)—N(3)—O(2)	117.9 (3)	118.7 (3)	119.0 (4)	118.7 (4)	118.7 (2)
O(1)—N(3)—O(2)	123.2 (3)	122.4 (2)	122.8 (4)	121.9 (4)	122.7 (3)
C(1)—N(1)—C(8)	120.5 (3)	121.5 (3)	123.9 (3)	124.2 (3)	124.4 (3)
C(1)—N(1)—C(9)	121.1 (3)	120.6 (3)	119.8 (3)	119.6 (4)	121.6 (2)
C(8)—N(1)—C(9)	118.3 (3)	117.7 (3)	116.3 (4)	116.0 (4)	113.2 (3)
N(1)—C(1)—C(10)	—	—	117.4 (3)	117.2 (3)	119.3 (2)
N(2)—C(1)—C(10)	—	—	123.9 (3)	124.5 (3)	116.4 (2)
C(1)—C(10)—C(11)	—	—	—	—	109.5 (2)
C(1)—C(10)—C(12)	—	—	—	—	113.0 (3)
C(1)—C(10)—C(13)	—	—	—	—	108.1 (2)
C(11)—C(10)—C(12)	—	—	—	—	111.9 (3)
C(11)—C(10)—C(13)	—	—	—	—	107.0 (3)
C(12)—C(10)—C(13)	—	—	—	—	107.0 (3)
N(1)—C(1)—N(2)—C(2)	-177.9 (3)	-174.4 (3)	-171.2 (4)	170.4 (4)	20.7 (3)
C(1)—N(2)—C(2)—C(3)	-155.4 (3)	-152.0 (3)	57.5 (5)	121.7 (5)	-137.5 (3)
C(4)—C(5)—N(3)—O(2)	8.7 (3)	5.8 (3)	-5.7 (4)	6.7 (5)	-179.2 (3)
N(2)—C(1)—N(1)—C(9)	0.5 (4)	3.5 (4)	3.3 (5)	-8.4 (5)	25.4 (3)
C(9)—N(1)—C(1)—C(10)	—	—	-179.3 (5)	175.0 (5)	-149.7 (3)
N(1)—C(1)—C(10)—C(12)	—	—	—	—	31.0 (3)
N(2)—C(1)—C(10)—C(13)	—	—	—	—	-26.3 (3)

bond and 0.9 in all five molecules for C(1)—N(2), indicating the least N—C—N π -type delocalization in (III). The C(1)—N(1) bonds are, therefore, intermediate between single and double bonds, while the C(1)—N(2) bonds are typical double bonds. The difference between the C(1)—N(1) and C(1)—N(2) bonds increases with the size of the substituent at C(1). The C(1)—C(10) bond lengths of 1.504 (6) Å in both molecules of (II) are typical of the C_{sp^2} — C_{sp^3} distance in acetamidines. In (III) this bond is much longer [1.538 (3) Å] due to steric effects.

Two isomeric forms are possible depending on the disposition of the substituents at the amidine C=N² double bond. The substituent at N² can be positioned *trans* or *cis* to the N¹ atom. The molecules of (I) and (II) are in *trans* configuration, and only the molecule of (III) adopts *cis* configuration, forced by the bulky *tert*-butyl substituent at C(1). The most bulky groups bonded to N¹, N² or C(1) are always in *trans* position.

That situation was found in N¹,N¹-(2,6-dimethylpentamethylene)-N²-phenyl-2,2-dimethylpropanamide (Gilli & Bertolasi, 1979). The *cis* configuration was also found in unsubstituted acetamide (Norrestam *et al.*, 1983) and in N²-*p*-nitrophenylbenzamide (Surma *et al.*, 1988).

In all *cis* amidines the N¹—C—N² angle is wider than in *trans* derivatives. The situation in the present structures is illustrated in Fig. 2. The value of 118° is typical for the majority of C(1)-substituted *trans* amidines investigated so far (Ciszak, Gdaniec & Kosturkiewicz, 1987) and the molecules of (II) [118.7 (3) and 118.2 (3)°] belong to that group. The widening of this angle in the present formamide derivative (I) [123.6 (3) and 123.2 (3)°] can be recognized as being due to the small volume of the H atom situated at C(1). In *trans* formamidines and in all *cis* amidines this angle is widened to values larger than 120°. It equals 124.2 (2)° in (III), 125.5 (1)° in

acetamidine (Norrestam *et al.*, 1983) and $125.9(3)^\circ$ in *N*²-*p*-nitrophenylbenzamidine (Surma *et al.*, 1988). The sum of bond angles around N(1) is $359.9(7)^\circ$ (mean) in (I), $359.7(7)^\circ$ (mean) in (II) and $359.3(3)^\circ$ in (III).

The Winkler & Dunitz (1971) parameters characterizing the out-of-plane deformations of the amine group, χ_C and χ_N , indicate small deviations from planarity with the exception of N(1) in (III) [-10.6°] which shows non-planarity. The values of τ show that the twist about the C(1)–N(1) bond is minimal in (I), small in (II) and large in (III) (-1.8 and -0.7° , 2.4 and -4.4° , and 33.2° , respectively). As calculated by CNDO/2, the differences in torsion angles between molecules *A* and *B* in the asymmetric unit of (I) lead to the conformations with the same total energy ($-3924 \text{ eV} \approx -0.63 \text{ fJ}$) for both molecules. The large τ in (III) is evidently due to molecular overcrowding. This overcrowding is further illustrated by the twist of the phenyl groups relative to the amidine plane. The angles which the formamidine and acetamidine groups make with the phenyl ring [$26.8(4)$ and $32.7(4)^\circ$; $61.3(2)$ and $70.7(4)^\circ$, respectively] are significantly different as a result of substitution of H(1) by the methyl group while the *trans* configuration is retained. A somewhat reduced interplanar angle could be reached in the 2,2-dimethylpropane derivative (III) [$59.2(3)^\circ$] where the configuration has been changed to the *cis* form.

The molecular packing is shown in Fig. 3. The packing of (I) is characterized by layers of molecules *A* ($y = \frac{1}{2}, \frac{3}{2}, \dots$) and *B* ($y = 0, 1, \dots$) alternating in the **b** direction. Packing of (II) shows layers of molecules *A* ($z = \frac{1}{2}, \frac{3}{2}, \dots$) and *B* ($z = 0, 1, \dots$) alternating in the **c** direction. In both crystals the amidine groups in the neighboring layers are almost perpendicular [$84.0(4)^\circ$ in (I) and $85.9(4)^\circ$ in (II)].

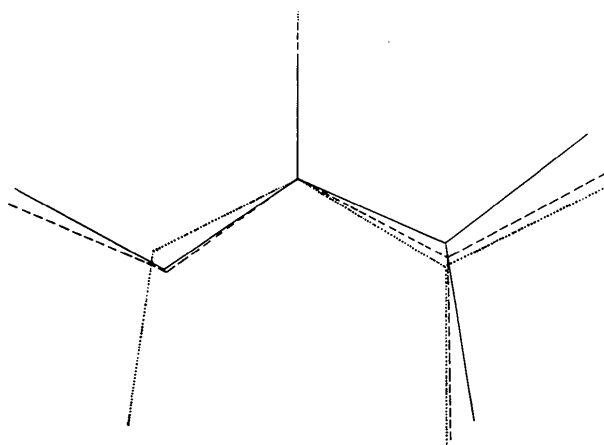


Fig. 2. Best fit (Nyburg, 1987) of the substituted amidine fragment of the present three amidines: full line – averaged formamidine [(I)*A* and (I)*B*], broken line – averaged acetamidine [(II)*A* and (II)*B*], and dotted line – 2,2-dimethylpropanamide (III).

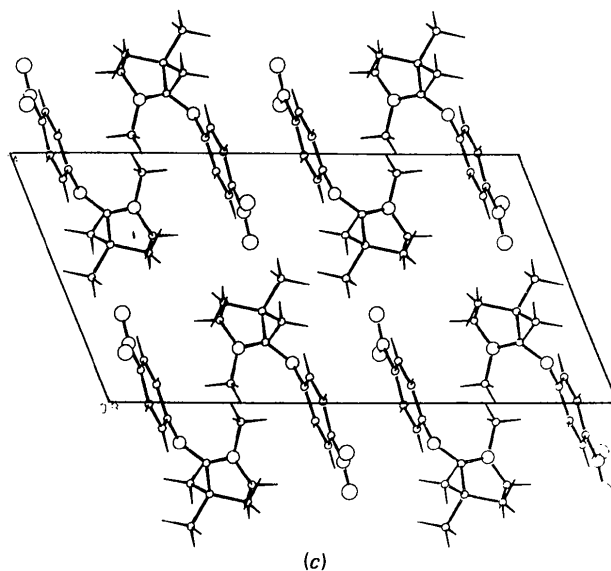
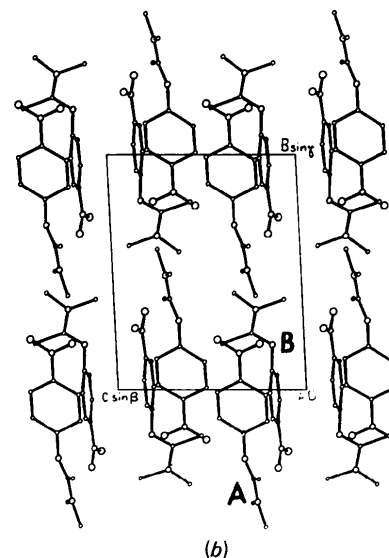
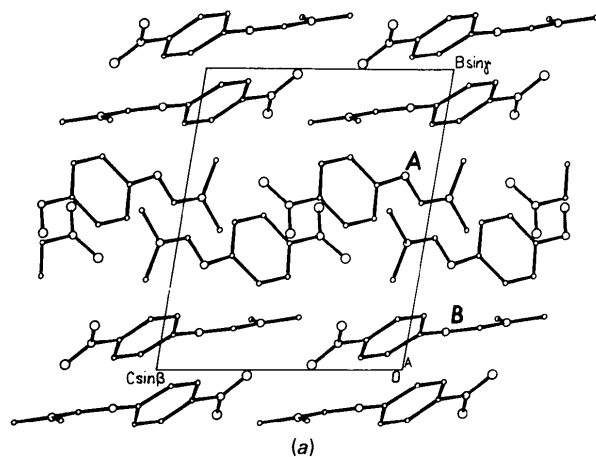


Fig. 3. Projections of the crystal structures of (a) (I) along **a**, (b) (II) along **a**, (c) (III) along **b**.

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(+)-(1*S*,3*S*)-1-Bromo-3-(bromomethyl)-1,2,2-trimethylcyclohexane. X-ray Structure at 123 K, NMR Spectrum and Molecular Mechanics Calculations

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Abstract. The structure of the title compound has been redetermined from low temperature X-ray data. C₁₀H₁₈Br₂, *M_r* = 298.07, orthorhombic, *P*2₁2₁2₁, *a* = 8.435 (1), *b* = 10.345 (2), *c* = 12.944 (3) Å, *V* = 1129.5 Å³, *Z* = 4, *D_x* = 1.75 g cm⁻³, λ(Mo Kα) = 0.71073 Å, μ = 70.6 cm⁻¹, *F*(000) = 592, *T* = 123 K, *R* = 0.024, *wR* = 0.033, *S* = 1.24 for 1380 unique observed reflections. Comparison of observed ¹H NMR parameters with those calculated from the Karplus equation based on the observed structure confirm that the solid and solution phase structures are identical. This indicates that the solution species is restricted in conformational freedom. Theoretical calculations (MMX) indicate that the observed conformation is the most favorable. Δ*H_f* is almost the same for the *cis* and *trans* isomers confirming the previously postulated mechanism for product formation.

Introduction. We have recently reported the synthesis and characterization of (+)-(1*S*,3*S*)-1-bromo-3-(bromomethyl)-1,2,2-trimethylcyclohexane (Longton, Bagrodia, Lutz, Pinkerton & Fry, 1987). A full characterization of this compound is important to us in

the design of strategies for asymmetric synthesis. In our original report we described an approximate structure for this compound based on room temperature X-ray data. The structure was however poorly defined due to the high volatility of this material (small data set due to sublimation of the crystal, high thermal parameters and no observed hydrogen positions).

The result of this study showed that only the *trans* isomer (axial 1-bromo, equatorial 3-bromomethyl) was formed in the synthesis. Using calculated hydrogen positions based on the approximate carbon skeleton coupled with ¹H NMR data, it appeared that the conformation of the bromomethyl group was the same in solution as in the solid state. This implies conformational rigidity with restricted rotation of this substituent in solution.

We have since obtained much better X-ray data measured at 123 K and re-refined the structure. We have also carried out molecular mechanics calculations (Serena Software, 1986) on the different possible rotamers of the bromomethyl group to confirm that the observed structure has the lowest energy. In addition we have carried out the same calculations for the *cis*