

## Structures of Two Guanidine Derivatives

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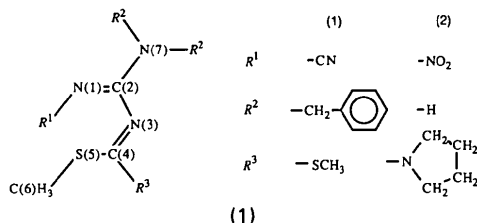
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**Abstract.** (1) *N*-[(1,1-Dibenzyl-2-cyano)amidino]-dithiocarbonylimidic acid dimethyl ester,  $C_{19}H_{20}N_4S_2$ ,  $M_r = 368.53$ , monoclinic,  $P2_1/c$ ,  $a = 11.849$  (4),  $b = 9.598$  (3),  $c = 16.906$  (9) Å,  $\beta = 97.71$  (4)°,  $V = 1905.30$  (1.33) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.28$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 2.76$  cm<sup>-1</sup>,  $F(000) = 776$ ,  $T = 298$  K,  $R = 0.041$  for 3118 unique observed reflections with  $I > \sigma(I)$ . (2) 2-Methyl-3-(2-nitroamidino)-1,1-tetramethyleneisothiourea,  $C_7H_{13}N_5O_2S$ ,  $M_r = 231.28$ , monoclinic,  $P2_1/c$ ,  $a = 9.804$  (3),  $b = 11.315$  (4),  $c = 10.190$  (3) Å,  $\beta = 111.66$  (2)°,  $V = 1050.44$  (55) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.46$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 2.85$  cm<sup>-1</sup>,  $F(000) = 488$ ,  $T = 298$  K,  $R = 0.034$  for 1786 unique observed reflections with  $I > \sigma(I)$ . In both molecules the backbone is markedly nonplanar to reduce nonbonded intramolecular contacts. The site of the major twist, which reaches  $-60.0$  (3)° in a nominal double bond in the thiourea part of (2), is consistent with resonance structures based on the better electron-donor ability of the  $-\text{NC}_4\text{H}_8$  group in (2) relative to that of  $-\text{SCH}_3$  in (1).

**Introduction.** The structures of compounds (1) and (2) were determined as part of a program of comparison of the properties of double bonds in push-pull systems. Here N(7) and R<sup>3</sup> are the main electron-pair donors, R<sup>1</sup> is the acceptor. Atoms N(7), C(2), N(1) comprise the amidino group. Atoms S(5), S(12) in R<sup>3</sup>, C(4) and N(3) form the dithiocarbonylimidic acid group of (1); atoms N(3), S(5), C(4) and N(8) in R<sup>3</sup> form the isothiourea group of (2).



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**Experimental.** Preparation of (1) by reaction of dibenzylcyanoguanidine with carbon disulfide, followed by methylation (Evers & Fischer, 1979). Reaction of nitroguanidine under the same conditions yielded nitroguanyldithiocarbonylimidic acid dimethyl ester, which subsequently reacted with pyrrolidine to yield (2) (Evers, 1981). Colorless single crystals mounted on glass fiber with quick-setting epoxy cement. Nicolet R3m/E diffractometer system, graphite monochromator, unit-cell parameters by least-squares refinement of 25 reflections [ $23 < 2\theta < 35^\circ$  for (1),  $24 < 2\theta < 26^\circ$  for (2)],  $\theta$ - $2\theta$  scans at variable rates (6.0–29.3° min<sup>-1</sup>),  $2\theta_{\text{max}} = 50^\circ$ , three reflections monitored every 97 reflections, negligible decrease in intensity over the course of data collection, no absorption correction, observed reflections with  $I > \sigma(I)$  used for refinement. Structure by direct methods; all H atoms appeared on difference maps but were inserted in ideal positions and not refined [except H(7a) and H(7b) of molecule (2), for which only interatomic distances were constrained], all C–H bond lengths fixed at 0.96 Å; anisotropic thermal parameters for all except H atoms, and fixed isotropic parameters for H atoms (about 20% greater than that of carrying atom). Refined by cascade block-diagonal least squares on  $F$ , about 100 parameters per block chosen automatically on the basis of type of parameter and the shift/e.s.d. ratio, atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations were performed on a Data General Eclipse S140 computer using the *SHELXTL* (Sheldrick, 1985) program package.

(1) Irregular crystal approximately  $0.34 \times 0.50 \times 0.78$  mm, index range  $0 \leq h \leq 14$ ,  $0 \leq k \leq 11$ ,  $-20 \leq l \leq 19$ , 3378 measured unique intensities,  $R_{\text{int}} = 0.010$ , 3118 unique observed data used for refinement, refinement of 227 parameters converged to  $R = 0.041$ ,  $wR = 0.043$ ,  $w = 1/[\sigma^2(F) + 0.00012F^2]$  where  $\sigma^2(F)$  is from counting statistics, goodness of fit = 1.89,  $|\Delta/\sigma|_{\text{max}} = 0.07$  in final cycle; highest

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peak in final difference map  $0.20$ , lowest hole  $-0.17 \text{ e } \text{Å}^{-3}$ .

(2) Irregular crystal approximately  $0.32 \times 0.60 \times 0.72 \text{ mm}$ , index range  $0 \leq h \leq 11$ ,  $0 \leq k \leq 13$ ,  $-12 \leq l \leq 11$ , 1858 measured unique intensities (not including space-group absences),  $R_{\text{int}} = 0.007$ , 1786 unique observed data used for refinement, refinement of 146 parameters converged to  $R = 0.034$ ,  $wR = 0.046$ ,  $w = 1/[\sigma^2(F) + 0.00010F^2]$  where  $\sigma^2(F)$  is from counting statistics, goodness of fit = 2.81,  $|\Delta/\sigma|_{\text{max}} = 0.04$  in final cycle; highest peak in final difference map  $0.22$ , lowest hole  $-0.18 \text{ Å}^{-3}$ .

**Discussion.** Thermal ellipsoid plots of the molecules are shown in Figs. 1 and 2, which also indicate the numbering system used in the structure determination. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, bond lengths in Table 2.\*

Molecule (1) has roughly the configuration shown by the structural formula: the bond  $\text{N}(1)\text{—C}(10)$  (in  $R^1$ ) lies approximately *trans* to  $\text{C}(2)\text{—N}(7)$  to avoid the bulky  $R^2$  group;  $\text{S}(5)\text{—C}(6)$  is then approximately *trans* to  $\text{C}(4)\text{—N}(3)$  to avoid  $R^1$ . In molecule (2), the corresponding bonds are shifted to approximately *cis* configurations so that  $\text{C}(6)$  can avoid the bulkier  $R^3$  group; the smaller  $R^2$  allows  $R^1$  to move away from  $\text{C}(6)$ .

In view of the resonance structures that move electrons from donor groups  $\text{N}(7)$  and  $R^3$  to the acceptor group  $R^1$ , the backbone, consisting of atoms  $\text{N}(1)$ ,  $\text{C}(2)$ ,  $\text{N}(3)$ ,  $\text{C}(4)$ ,  $\text{S}(5)$  and  $\text{N}(7)$ , is expected to be as nearly planar as nonbonded contacts permit. In fact, these contacts cause the backbones of both molecules to twist markedly out of planar configuration. Molecule (1) twists to move  $\text{S}(5)$  away from  $\text{N}(1)$  by positioning the  $\text{S}$  atom below the plane of the backbone at similar distances from  $\text{N}(1)$  and  $\text{N}(7)$  [ $\text{S}(5)\cdots\text{N}(1)$   $3.470(3)$ ,  $\text{S}(5)\cdots\text{N}(7)$   $3.607(1) \text{ Å}$ ]. Molecule (2) twists to move  $\text{C}(6)$  away from  $\text{N}(1)$  by positioning  $\text{C}(6)$  above the backbone at similar distances from  $\text{N}(1)$ ,  $\text{C}(2)$  and  $\text{N}(3)$  [ $\text{C}(6)\cdots\text{N}(1)$   $3.178(2)$ ,  $\text{C}(6)\cdots\text{C}(2)$   $3.176(3)$ ,  $\text{C}(6)\cdots\text{N}(3)$   $3.026(3) \text{ Å}$ ].

Most of the out-of-plane twist occurs about the nominal single bond  $\text{C}(2)\text{—N}(3)$  or the nominal double bond  $\text{N}(3)\text{—C}(4)$  according to which has less double-bond character in the actual molecule. The dihedral angle from the best plane through atoms  $\text{N}(1)$ ,  $\text{C}(2)$ ,  $\text{N}(3)$ ,  $\text{N}(7)$  to the plane of  $\text{C}(2)$ ,  $\text{N}(3)$ ,

$\text{C}(4)$  is  $82.2(3)^\circ$  in (1) with  $\text{C}(2)\text{—N}(3)$   $1.385(2) \text{ Å}$ ,  $-8.2(1.4)^\circ$  in (2) with  $\text{C}(2)\text{—N}(3)$   $1.324(2) \text{ Å}$ . Both the dihedral angles and bond lengths indicate more double-bond character for  $\text{C}(2)\text{—N}(3)$  in (2). The dihedral angle from the plane of  $\text{C}(2)$ ,  $\text{N}(3)$ ,  $\text{C}(4)$  to the plane defined by  $\text{N}(3)$ ,  $\text{C}(4)$ ,  $\text{S}(5)$ ,  $\text{S}(12)$  in (1) is  $3.0(6)^\circ$  with  $\text{N}(3)\text{—C}(4)$   $1.275(2) \text{ Å}$ , to the plane defined by  $\text{N}(3)$ ,  $\text{C}(4)$ ,  $\text{S}(5)$ ,  $\text{N}(8)$  in (2) is  $-60.0(3)^\circ$  with  $\text{N}(3)\text{—C}(4)$   $1.331(2) \text{ Å}$ . Hence the angles and bond lengths indicate that there is more double-bond character in the  $\text{N}(3)\text{—C}(4)$  bond in (1). These differences appear to be the result of the fact that (2) contains a better electron acceptor

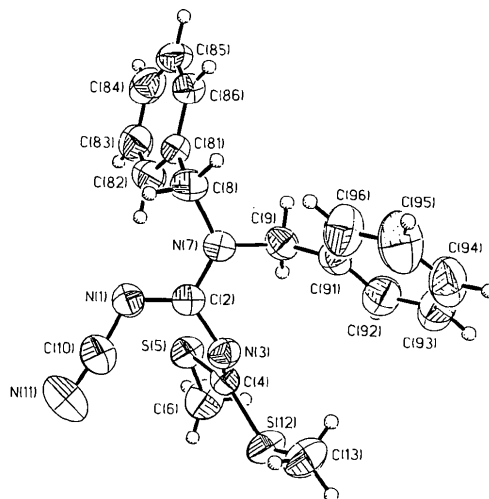


Fig. 1. Thermal ellipsoid (50% probability) plot of (1). H atoms are shown as small spheres of arbitrary radius. The molecule is rotated  $15^\circ$  to the right from the view normal to the best plane through  $\text{N}(1)$ ,  $\text{C}(2)$ ,  $\text{N}(3)$ ,  $\text{N}(7)$ .

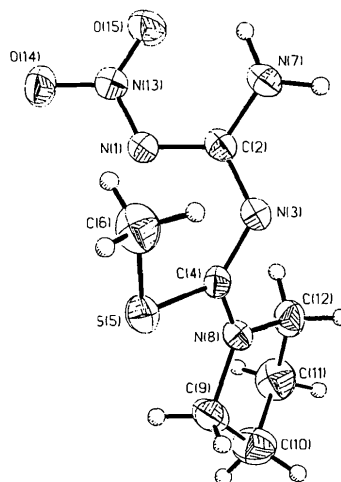


Table 1. Atom coordinates and temperature factors ( $\text{\AA}^2$ ) for (1) and (2)

	x	y	z	$U^*$
(1)				
N(1)	0.1507 (1)	0.3182 (1)	0.1029 (1)	0.054 (1)
C(2)	0.1967 (1)	0.4299 (2)	0.1390 (1)	0.046 (1)
N(3)	0.2815 (1)	0.5076 (2)	0.1109 (1)	0.050 (1)
C(4)	0.2590 (1)	0.6038 (2)	0.0591 (1)	0.048 (1)
S(5)	0.1187 (1)	0.6514 (1)	0.0232 (1)	0.057 (1)
C(6)	0.1306 (2)	0.7947 (2)	-0.0427 (1)	0.082 (1)
N(7)	0.1686 (1)	0.4661 (1)	0.2103 (1)	0.049 (1)
C(8)	0.0933 (2)	0.3781 (2)	0.2516 (1)	0.060 (1)
C(9)	0.2045 (1)	0.6001 (2)	0.2472 (1)	0.054 (1)
C(10)	0.1845 (2)	0.2767 (2)	0.0350 (1)	0.062 (1)
N(11)	0.2060 (2)	0.2284 (2)	-0.0231 (1)	0.093 (1)
S(12)	0.3681 (1)	0.6949 (1)	0.0220 (1)	0.071 (1)
C(13)	0.4915 (2)	0.6233 (3)	0.0814 (1)	0.086 (1)
C(81)	-0.0231 (1)	0.4401 (2)	0.2524 (1)	0.050 (1)
C(82)	-0.0853 (2)	0.4924 (2)	0.1839 (1)	0.062 (1)
C(83)	-0.1945 (2)	0.5426 (2)	0.1840 (1)	0.072 (1)
C(84)	-0.2426 (2)	0.5409 (2)	0.2535 (2)	0.078 (1)
C(85)	-0.1812 (2)	0.4913 (2)	0.3225 (1)	0.075 (1)
C(86)	-0.0726 (2)	0.4410 (2)	0.3220 (1)	0.062 (1)
C(91)	0.3232 (1)	0.6041 (2)	0.2918 (1)	0.052 (1)
C(92)	0.3920 (2)	0.7155 (2)	0.2829 (1)	0.075 (1)
C(93)	0.4983 (2)	0.7281 (3)	0.3273 (2)	0.097 (1)
C(94)	0.5363 (2)	0.6283 (3)	0.3804 (2)	0.099 (1)
C(95)	0.4697 (2)	0.5171 (3)	0.3900 (2)	0.110 (1)
C(96)	0.3629 (2)	0.5038 (2)	0.3462 (1)	0.084 (1)
(2)				
N(1)	1.0338 (1)	0.9095 (1)	0.1943 (1)	0.035 (1)
C(2)	1.0973 (2)	1.0073 (1)	0.2726 (2)	0.032 (1)
N(3)	1.2397 (1)	1.0017 (1)	0.3485 (1)	0.037 (1)
C(4)	1.3187 (2)	0.9033 (1)	0.3642 (2)	0.031 (1)
S(5)	1.2944 (1)	0.7727 (1)	0.4471 (1)	0.041 (1)
C(6)	1.1507 (2)	0.8101 (2)	0.5082 (2)	0.052 (1)
N(7)	1.0274 (2)	1.1063 (1)	0.2809 (2)	0.044 (1)
N(8)	1.4345 (1)	0.9041 (1)	0.3296 (1)	0.033 (1)
C(9)	1.5464 (2)	0.8101 (2)	0.3603 (2)	0.044 (1)
C(10)	1.6593 (2)	0.8587 (2)	0.3061 (2)	0.057 (1)
C(11)	1.5795 (2)	0.9510 (2)	0.1986 (2)	0.057 (1)
C(12)	1.4679 (2)	1.0031 (1)	0.2517 (2)	0.041 (1)
N(13)	0.8985 (1)	0.9182 (1)	0.0975 (1)	0.036 (1)
O(14)	0.8396 (1)	0.8233 (1)	0.0444 (1)	0.054 (1)
O(15)	0.8326 (1)	1.0129 (1)	0.0562 (1)	0.055 (1)

\* Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

—NO<sub>2</sub> and especially a better electron donor —NC<sub>4</sub>H<sub>8</sub>, with the consequence that structures having a double bond between C(2) and N(3) and a single bond between N(3) and C(4) are enhanced relative to (1). The large out-of-plane twist about N(3)—C(4) in (2) is in the range found for other

Table 2. Bond lengths ( $\text{\AA}$ ) for (1) and (2)

(1)			
N(1)—C(2)	1.315 (2)	N(1)—C(10)	1.327 (3)
C(2)—N(3)	1.385 (2)	C(2)—N(7)	1.340 (2)
N(3)—C(4)	1.275 (2)	C(4)—S(5)	1.752 (2)
C(4)—S(12)	1.745 (2)	S(5)—C(6)	1.788 (2)
N(7)—C(8)	1.471 (2)	N(7)—C(9)	1.467 (2)
C(8)—C(81)	1.505 (3)	C(9)—C(91)	1.505 (2)
C(10)—N(11)	1.145 (3)	S(12)—C(13)	1.796 (2)
C(81)—C(82)	1.381 (2)	C(81)—C(86)	1.382 (3)
C(82)—C(83)	1.382 (3)	C(83)—C(84)	1.372 (3)
C(84)—C(85)	1.376 (3)	C(85)—C(86)	1.375 (3)
C(91)—C(92)	1.365 (3)	C(91)—C(96)	1.370 (3)
C(92)—C(93)	1.383 (3)	C(93)—C(94)	1.348 (4)
C(94)—C(95)	1.350 (4)	C(95)—C(96)	1.384 (3)
(2)			
N(1)—C(2)	1.371 (2)	N(1)—N(13)	1.333 (2)
C(2)—N(3)	1.324 (2)	C(2)—N(7)	1.332 (2)
N(3)—C(4)	1.331 (2)	C(4)—S(5)	1.762 (2)
C(4)—N(8)	1.307 (2)	S(5)—C(6)	1.789 (3)
N(8)—C(9)	1.477 (2)	N(8)—C(12)	1.478 (2)
C(9)—C(10)	1.511 (3)	C(10)—C(11)	1.507 (3)
C(11)—C(12)	1.507 (3)	N(13)—O(14)	1.244 (2)
N(13)—O(15)	1.242 (2)		

sterically hindered push-pull systems (Gilardi, Flippin-Anderson & George, 1989).

H atoms H(7a) and H(7b) in (2) were refined with N...H and H...H distances constrained to 0.96 and 1.663  $\text{\AA}$ . The distance O(15)...H(7a) 1.987 (13)  $\text{\AA}$  indicates a hydrogen bond, with bond angle at H(7a) 120.0 (8)°.

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## References

- EVERS, R. (1981). *Z. Chem.* **21**, 358–360.  
 EVERS, R. & FISCHER, E. (1979). GDR Patent 137 929; *Chem. Abstr.* (1980), **92**, 180848p.  
 GILARDI, R., FLIPPIN-ANDERSON, J. & GEORGE, C. (1989). *Am. Crystallogr. Assoc. Meet.*, Seattle, July, Abstract PB06.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 SHELDRICK, G. M. (1985). *SHELXTL Users Manual*. Revision 5.1 Nicolet XRD Corporation, Madison, Wisconsin, USA.

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## Structures of 1,2,3-Triazine Derivatives

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**Abstract.** (I) 4-Methyl-6-phenyl-1,2,3-triazine, C<sub>10</sub>H<sub>9</sub>N<sub>3</sub>,  $M_r = 171.2$ , monoclinic,  $P2_1/c$ ,  $a = 10.684$  (1),  $b = 13.755$  (1),  $c = 6.074$  (1)  $\text{\AA}$ ,  $\beta =$

$103.28$  (1)°,  $U = 868.8$  (2)  $\text{\AA}^3$ ,  $Z = 4$ ,  $D_x = 1.309$  Mg m<sup>-3</sup>,  $\mu = 0.667$  mm<sup>-1</sup>,  $F(000) = 360$ ,  $R = 0.055$  for 909 reflexions. (II) 4-Phenylcyclohexa-