

***N,N'*-Bis(1-methylethyl)-6-methylthio-1,3,5-triazine-2,4-diamine, Prometryn, C<sub>10</sub>H<sub>19</sub>N<sub>5</sub>S**

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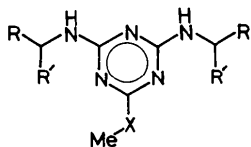
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**Abstract.**  $M_r = 241.3$ , triclinic,  $P\bar{1}$ ,  $a = 10.094$  (3),  $b = 11.834$  (2),  $c = 12.370$  (2) Å,  $\alpha = 79.08$  (1),  $\beta = 79.73$  (2),  $\gamma = 77.12$  (2)°,  $V = 1400.0$  (5) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.14$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.22$  mm<sup>-1</sup>,  $F(000) = 520$ ,  $T = 293$  K,  $R = 0.074$  for 1740 unique reflections. The two independent molecules of the triazine herbicide in the asymmetric unit are very similar with the thiomethyl group and the first two atoms of the amine side chains approximately coplanar with the triazine ring system. The bond lengths and angles in the triazine ring are similar to those in unsubstituted triazine, with small C–N–C angles and large N–C–N angles.

**Introduction.** As an extension to a study of important herbicides such as the phenoxyalkanoic acids (Smith & Kennard, 1979), the structural chemistry of chemical triazine herbicides is being studied.



- |    |                           |              |
|----|---------------------------|--------------|
| 1. | R = R' = Me<br>X = S      | } Prometryn  |
| 2. | R = Me<br>R' = H<br>X = S | } Simetryne® |
| 3. | R = Me<br>R' = H<br>X = O | } Simetone   |
| 4. | R = R' = Me<br>X = O      | } Prometone  |

These include prometone [*N,N'*-bis(1-methylethyl)-6-methoxy-1,3,5-triazine-2,4-diamine] (Graham, Akrigg & Sheldrick, 1977), Simetryne® [*N,N'*-diethyl-6-methylthio-1,3,5-triazine-2,4-diamine] (Graham, Akrigg & Sheldrick, 1978*a*) and simetone [*N,N'*-diethyl-6-methoxy-1,3,5-triazine-2,4-diamine] (Graham, Akrigg & Sheldrick, 1978*b*). The title compound, prometryn, is a member of this 1,3,5-triazine series and is described by Gysin (1962). It is known as 2,4-bis(isopropylamino)-6-methylthio-1,3,5-triazine and is available under various commercial names, e.g. G 34161, Gesagard and Caparol (Spencer, 1973). Triazines were originally

developed by J. R. Geigy SA of Basle and find use as selective herbicides in corn (Ashton & Crafts, 1981). These compounds affect the photosynthetic pathway involving non-cyclic photophosphorylation by stopping electron flow between the quinone (Q) and cytochrome  $b_{559}$  low potential (LP) stages in the Cyclic II synthetic route (Goodwin & Mercer, 1982).

**Experimental.** EPA (Environmental Protection Agency) analytical standard, recrystallized from ethanol; X-ray data collected from one crystal (0.50 × 0.12 × 0.08 mm) for a hemisphere of reciprocal lattice (max.  $\sin\theta/\lambda$  0.54 Å<sup>-1</sup>), 16 high-angle reflections ( $2\theta$  23–27°) used to measure lattice parameters; 3914 unique reflections,  $R_{\text{int}} 0.03$ , 1740 with  $I > 2\sigma(I)$  used in structure analysis;  $h$  0–10,  $k$  ±12,  $l$  ±13; standards 155 382 (32); 266 943 (49); 451 1003 (60); Enraf–Nonius CAD-4  $\kappa$  diffractometer ( $2\theta$ – $\omega$  scanning mode), graphite-monochromatized Mo  $K\alpha$ ; no absorption correction; reflection 100 suffered from extinction and was removed from data set; trial structure obtained using both sharpened Patterson synthesis and symbolic addition direct methods; H determined from difference Fourier synthesis; full-matrix refinement on  $F$  of non-hydrogen atoms (anisotropic, H isotropic,  $U = 0.05$  Å<sup>2</sup>) gave  $R = 0.074$  and  $wR = 0.076$ ,  $w = 2.9/[\sigma^2(F_o) + 0.0025F_o^2]$ ; all  $\Delta/\sigma < 0.5$ ; final difference Fourier map showed no peaks  $> 0.2$  e Å<sup>-3</sup>; all computations completed using SHELX76 (Sheldrick, 1976) on a Prime 550 computer; neutral atom scattering factors [non-hydrogen (Cromer & Mann, 1968), corrected for anomalous scattering, and hydrogen atoms (Stewart, Davidson & Simpson, 1965)]. Atomic coordinates\* are listed in Table 1.

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42061 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )

$U_{\text{eq}}$  is defined as  $(U_{11}U_{22}U_{33})^{1/3}$ .

|       | Molecule A |           |           |                 | Molecule B |            |           |                 |
|-------|------------|-----------|-----------|-----------------|------------|------------|-----------|-----------------|
|       | x          | y         | z         | $U_{\text{eq}}$ | x          | y          | z         | $U_{\text{eq}}$ |
| C(11) | 2220 (10)  | 6180 (8)  | 4710 (8)  | 97 (5)          | -2118 (11) | -1082 (9)  | 5934 (9)  | 115 (6)         |
| S(1)  | 2122 (3)   | 4672 (2)  | 5092 (2)  | 91 (1)          | -1753 (3)  | 217 (2)    | 6297 (3)  | 92 (1)          |
| C(1)  | 957 (8)    | 4670 (8)  | 6335 (7)  | 62 (4)          | -116 (8)   | -265 (8)   | 6673 (7)  | 69 (4)          |
| N(2)  | 615 (7)    | 3638 (5)  | 6736 (6)  | 63 (3)          | 464 (8)    | 607 (5)    | 6779 (6)  | 68 (3)          |
| C(3)  | -356 (9)   | 3649 (6)  | 7625 (7)  | 56 (4)          | 1785 (10)  | 252 (7)    | 6974 (7)  | 66 (4)          |
| N(4)  | -947 (7)   | 4589 (5)  | 8138 (5)  | 63 (3)          | 2492 (7)   | -856 (5)   | 7128 (6)  | 65 (3)          |
| C(5)  | -455 (9)   | 5565 (6)  | 7659 (8)  | 62 (4)          | 1731 (11)  | -1630 (7)  | 7049 (7)  | 65 (4)          |
| N(6)  | 517 (7)    | 5649 (5)  | 6764 (6)  | 65 (3)          | 420 (8)    | -1397 (5)  | 6826 (6)  | 67 (4)          |
| N(3)  | 793 (7)    | 2643 (5)  | 8043 (6)  | 65 (3)          | 2458 (7)   | 1111 (5)   | 7021 (6)  | 73 (3)          |
| C(31) | -1779 (11) | 2482 (7)  | 9015 (8)  | 72 (4)          | 3911 (10)  | 935 (7)    | 7071 (9)  | 79 (5)          |
| C(32) | -1537 (13) | 1187 (10) | 9628 (11) | 143 (7)         | 4464 (14)  | 2040 (12)  | 6617 (13) | 170 (9)         |
| C(33) | -3235 (14) | 2795 (11) | 8790 (11) | 148 (8)         | 4296 (14)  | 442 (10)   | 8294 (11) | 149 (8)         |
| N(5)  | -935 (8)   | 6552 (6)  | 8099 (6)  | 79 (4)          | 2308 (8)   | -2784 (6)  | 7230 (7)  | 82 (4)          |
| C(51) | -1858 (14) | 6598 (7)  | 9153 (10) | 96 (6)          | 3641 (12)  | -3235 (8)  | 7608 (10) | 90 (5)          |
| C(52) | -3130 (19) | 6897 (19) | 9085 (14) | 271 (15)        | 4684 (18)  | -3317 (17) | 6634 (16) | 256 (13)        |
| C(53) | -1411 (18) | 7219 (26) | 9900 (17) | 324 (19)        | 3659 (18)  | -4460 (12) | 8366 (11) | 195 (10)        |

Table 2. Comparative geometrical data for the substituted triazines ( $\text{\AA}$  and deg)For prometryn, Simetryne<sup>®</sup>,  $X = \text{S}$ ; for prometone, simetone,  $X = \text{O}$ .

|                       | Prometryn  |            | Prometone <sup>a</sup> | Simetryne <sup>®b</sup> | Simetone <sup>c</sup> | Mean  |
|-----------------------|------------|------------|------------------------|-------------------------|-----------------------|-------|
|                       | A          | B          |                        |                         |                       |       |
| C(11)-X(1)            | 1.770 (9)  | 1.810 (11) | 1.431 (7)              | 1.810 (7)               | 1.440 (6)             | —     |
| X(1)-C(1)             | 1.754 (8)  | 1.739 (9)  | 1.340 (5)              | 1.764 (5)               | 1.358 (6)             | —     |
| C(1)-N(2)             | 1.324 (10) | 1.330 (11) | 1.319 (6)              | 1.324 (7)               | 1.306 (6)             | 1.321 |
| N(2)-C(3)             | 1.336 (11) | 1.356 (13) | 1.354 (5)              | 1.357 (7)               | 1.362 (6)             | 1.353 |
| C(3)-N(4)             | 1.353 (10) | 1.342 (11) | 1.352 (5)              | 1.332 (7)               | 1.337 (6)             | 1.343 |
| N(4)-C(5)             | 1.350 (10) | 1.346 (11) | 1.325 (5)              | 1.330 (7)               | 1.318 (6)             | 1.334 |
| C(5)-N(6)             | 1.346 (12) | 1.357 (10) | 1.357 (6)              | 1.360 (7)               | 1.361 (6)             | 1.356 |
| N(6)-C(1)             | 1.319 (11) | 1.319 (11) | 1.335 (5)              | 1.326 (7)               | 1.328 (6)             | 1.325 |
| C(3)-N(3)             | 1.341 (10) | 1.358 (11) | 1.332 (6)              | 1.346 (7)               | 1.332 (6)             | 1.342 |
| N(3)-C(31)            | 1.429 (12) | 1.445 (12) | 1.463 (7)              | 1.462 (8)               | 1.466 (6)             | 1.453 |
| C(31)-C(32)           | 1.561 (14) | 1.506 (16) | 1.528 (11)             | 1.497 (11)              | 1.496 (6)             | 1.518 |
| C(31)-C(33)           | 1.496 (17) | 1.592 (16) | 1.506 (11)             | —                       | —                     | —     |
| C(5)-N(5)             | 1.337 (10) | 1.353 (13) | 1.354 (6)              | 1.343 (7)               | 1.348 (6)             | 1.347 |
| N(5)-C(51)            | 1.463 (15) | 1.456 (14) | 1.451 (6)              | 1.457 (7)               | 1.462 (6)             | 1.458 |
| C(51)-C(52)           | 1.266 (23) | 1.454 (22) | 1.483 (9)              | 1.475 (11)              | 1.508 (8)             | 1.437 |
| C(51)-C(53)           | 1.466 (26) | 1.568 (16) | 1.523 (9)              | —                       | —                     | —     |
| C(11)-X(1)-C(1)       | 102.2 (4)  | 103.0 (5)  | 118.6 (4)              | 102.9 (3)               | 116.8 (4)             | —     |
| X(1)-C(1)-N(2)        | 113.7 (6)  | 113.1 (6)  | 113.2 (4)              | 113.4 (4)               | 112.4 (4)             | 113.2 |
| X(1)-C(1)-N(6)        | 119.3 (6)  | 119.9 (7)  | 118.6 (4)              | 118.7 (5)               | 118.3 (4)             | 119.0 |
| N(2)-C(1)-N(6)        | 127.0 (8)  | 126.7 (8)  | 128.1 (4)              | 127.9 (5)               | 129.2 (5)             | 127.8 |
| C(1)-N(2)-C(3)        | 114.2 (6)  | 113.6 (7)  | 113.6 (4)              | 113.2 (5)               | 112.6 (4)             | 113.4 |
| N(2)-C(3)-N(3)        | 117.2 (7)  | 116.3 (7)  | 116.4 (4)              | 116.3 (5)               | 115.4 (4)             | 116.3 |
| N(2)-C(3)-N(4)        | 125.8 (7)  | 126.9 (8)  | 125.3 (4)              | 125.8 (5)               | 125.9 (4)             | 125.9 |
| N(3)-C(3)-N(4)        | 116.9 (7)  | 116.8 (8)  | 118.3 (4)              | 117.9 (5)               | 118.7 (4)             | 117.7 |
| C(3)-N(3)-C(31)       | 124.8 (7)  | 124.8 (7)  | 125.6 (4)              | 123.8 (5)               | 124.4 (4)             | 124.7 |
| N(3)-C(31)-C(32)      | 111.9 (8)  | 111.8 (8)  | 108.8 (6)              | 112.0 (6)               | 112.2 (5)             | 111.3 |
| N(3)-C(31)-C(33)      | 113.9 (8)  | 113.2 (9)  | 110.1 (6)              | —                       | —                     | —     |
| C(32)-C(31)-C(33)     | 107.2 (9)  | 109.6 (9)  | 112.5 (6)              | —                       | —                     | —     |
| C(3)-N(4)-C(5)        | 113.1 (7)  | 111.6 (7)  | 113.7 (4)              | 114.3 (5)               | 113.6 (4)             | 113.3 |
| N(4)-C(5)-N(5)        | 119.1 (8)  | 117.5 (9)  | 118.8 (4)              | 118.8 (5)               | 118.2 (5)             | 118.5 |
| N(4)-C(5)-N(6)        | 125.9 (7)  | 127.7 (7)  | 127.2 (3)              | 126.1 (5)               | 127.2 (4)             | 126.8 |
| N(5)-C(5)-N(6)        | 115.0 (7)  | 114.8 (7)  | 114.0 (4)              | 115.0 (5)               | 114.6 (5)             | 114.7 |
| C(5)-N(5)-C(51)       | 123.0 (7)  | 123.8 (8)  | 125.1 (4)              | 125.1 (5)               | 123.3 (4)             | 124.1 |
| N(5)-C(51)-C(52)      | 116.3 (12) | 108.2 (11) | 112.5 (5)              | 113.2 (6)               | 111.7 (4)             | 112.4 |
| N(5)-C(51)-C(53)      | 112.4 (11) | 110.5 (9)  | 108.7 (5)              | —                       | —                     | —     |
| C(52)-C(51)-C(53)     | 113.5 (14) | 111.2 (11) | 112.4 (5)              | —                       | —                     | —     |
| C(11)-N(6)-C(5)       | 113.8 (6)  | 113.0 (7)  | 112.1 (4)              | 112.7 (5)               | 111.4 (4)             | 112.6 |
| N(6)-C(1)-X(1)-C(11)  | -5.6 (4)   | -11.7 (5)  | -2.5                   | +6.1                    | +0.9                  | —     |
| N(2)-C(1)-X(1)-C(11)  | +174.1 (5) | +168.4 (6) | +178.0                 | -175.7                  | -179.0                | —     |
| N(2)-C(3)-N(3)-C(31)  | +177.2 (8) | -171.3 (8) | +174.5                 | +177.9                  | -177.6                | —     |
| N(4)-C(3)-N(3)-C(31)  | -3.2 (8)   | +8.9 (8)   | +4.7                   | -3.8                    | +3.1                  | —     |
| N(4)-C(5)-N(5)-C(51)  | +7.2 (7)   | +6.2 (8)   | +6.6                   | +4.8                    | +6.7                  | —     |
| N(6)-C(5)-N(5)-C(51)  | -171.8 (7) | -172.6 (7) | -174.2                 | -177.6                  | -173.9                | —     |
| C(3)-N(3)-C(31)-C(32) | -150.6 (8) | +154.7 (8) | +120.6                 | —                       | +82.8                 | —     |
| C(3)-N(3)-C(31)-C(33) | +87.6 (8)  | -81.0 (8)  | -115.7                 | -85.2                   | —                     | —     |
| C(5)-N(5)-C(51)-C(52) | -94.9 (7)  | -90.9 (8)  | +88.6                  | +114.8                  | —                     | —     |
| C(5)-N(5)-C(51)-C(53) | +131.9 (7) | +147.1 (7) | -146.3                 | —                       | -84.8                 | —     |

References: (a) Graham, Akrigg &amp; Sheldrick (1977); (b) Graham, Akrigg &amp; Sheldrick (1978a); (c) Graham, Akrigg &amp; Sheldrick (1978b).

**Discussion.** There are two independent but similar molecules (*A* and *B*) of prometryn in the asymmetric unit. The atom numbering is shown in Fig. 1. The previously published structures of prometone, Simetryne® and simetone have been relabelled to conform with the convention used in Fig. 1. This scheme is based on the value of the torsion angle C(11)–X(1)–C(1)–N(2) being *ca* 180°. Comparative geometric data for these substituted triazines are in Table 2.

The *s*-triazine ring is essentially coplanar with the thiomethyl group and the first two atoms of the amine side chains. Another feature common to all members of this series of substituted triazines is the relatively high values of the residuals in the refinement, presumably due to high thermal motion in the amine side chains, particularly in the terminal alkyl groups. Despite these factors, the interatomic distances and angles are relatively consistent overall. The C(1)-*exo* angles are distorted [113.7 (6), 113.1 (6); 119.3 (6), 119.9 (7)°; group mean 113.2 (6), 119.0 (7)°] owing to the steric influence of the *S*-methyl group, the degree of distortion being independent of the nature of *X*. The coplanarity of the *X*-methyl group appears to be unaffected by the change from O to S. This is reflected in the torsion angle C(11)–X(1)–C(1)–N(2), which is not very different for the five determinations (*e.g.* for *X* = S, mean +172.5°; for *X* = O, mean +178.5°).

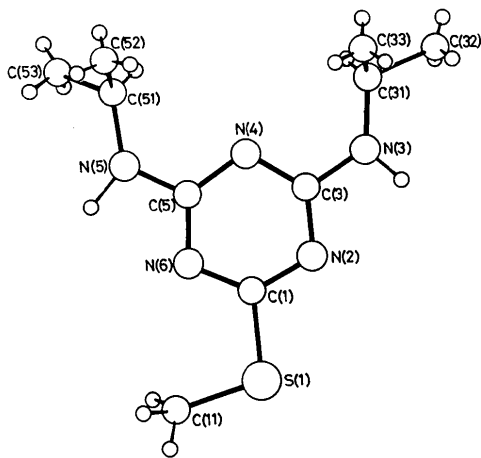


Fig. 1. Molecular conformation and atom numbering scheme for prometryn. Hydrogen atoms of the methyl groups are included at their calculated positions.

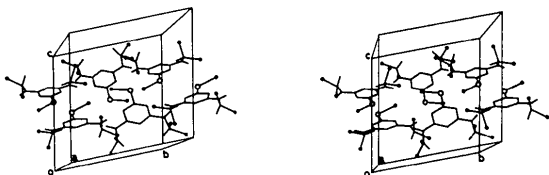


Fig. 2. Stereoview perpendicular to *bc*. (Open circles: S atoms, dots: CH<sub>3</sub> groups.)

Within the triazine ring, all C–N distances are similar [mean 1.339 (8) Å] while N–C–N angles are large [mean 126.8 (5)°] and C–N–C angles small [mean 113.1 (5)°]. These values are comparable with those found for the parent compound *s*-triazine (from both X-ray and neutron diffraction methods) (Wheatley, 1955; Coppens, 1967) [1.319 (5) Å; 126.8 (4); 113.2 (4)°] and emphasize the relative rigidity of this hetero ring system. In the amine side chains the angles about the nitrogens are quite distorted [mean 124.4 (6)°]. A characteristic of all these compounds is that both torsion angles N(4)–C(3)–N(3)–C(31) and N(4)–C(5)–N(5)–C(51) are close to 0°. Angles C(11)–S(1)–C(1) for both prometryn and Simetryne® are much smaller (mean 102.7°) than C(11)–O(1)–C(1) for prometone and simetone (mean 117.7°), which is an observation consistent with ether as against thioether systems. Packing of the molecules in the unit cell (Fig. 2) involves only N (both amine and hetero) in weak hydrogen bonding between *A* and *B* molecules in the asymmetric unit [N(3)*A*...N(6)*B* 3.03 (1) Å] and intra-unit associations [N(5)*A*...N(2)*B* 3.08 (1) Å (*x*, 1 + *y*, *z*); N(6)*A*...N(3)*B* 3.05 (1) Å (*x*, 1 + *y*, *z*)].

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