

The Structure of 2-Methyl-2*H*-naphtho[1,8-*de*]triazine

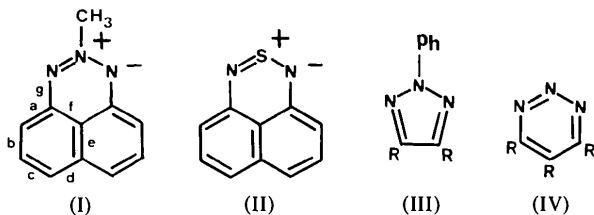
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Abstract. C₁₁H₉N₃, $M_r = 183.2$, monoclinic, $P2_1/c$, $a = 15.916$ (11), $b = 3.955$ (2), $c = 15.372$ (8) Å, $\beta = 112.83$ (3)°, $U = 892$ Å³, $Z = 4$, $D_c = 1.36$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.080$ mm⁻¹. $R = 0.057$ for 677 reflexions [$I > 3\sigma(I)$] and 164 parameters. Apart from the methyl group, which is rotated about the C–N bond, the molecule has *mm*2 symmetry within experimental error. Mean distances in the triazine ring are: C–N = 1.397 (6), N–N = 1.315 (6), C–C = 1.419 (6) Å, $\angle \text{CNN} = 114.2$ (5) and $\angle \text{NNN} = 132.5$ (7)°.

Introduction. The blue compound obtained by base-catalysed methylation of 1*H*-naphtho[1,8-*de*] [1,2,3]triazine was shown by Perkins (1964) to be 2-methyl-2*H*-naphtho[1,8-*de*]triazine (I).



A crystal $0.05 \times 1.5 \times 0.48$ mm was mounted about *b* and *hkl* intensities ($k = 0$ to 4) were measured on a computer-steered Supper diffractometer (Kryger, 1975) with monochromatic Mo $K\alpha$ radiation. 2446 independent reflexions were measured of which 677 had $I > 3\sigma(I)$. No correction was made for absorption. Cell dimensions were determined from 12 centred reflexions from a small crystal mounted on a Picker FACS1 diffractometer.

Examination of weighted reciprocal lattices revealed the orientation of the molecule. The *x* and *z* coordinates of the centre of the molecule were found by taking a few low-order *h0l* reflexions and moving the molecule systematically around the cell to find the position giving the lowest *R*. Packing considerations suggested that *y* was close to 0 or $\frac{1}{2}$.

For the possible solutions constrained refinements (Pawley, 1971) were carried out in which a scale factor, molecular centre and Euler angles were refined with 23

low-order reflexions. Conventional least-squares refinement of atomic coordinates, anisotropic thermal parameters, isotropic thermal parameters for H, a scale factor and an isotropic extinction coefficient, *g*, gave a final *R* of 0.057 ($R_w = 0.062$) for 164 parameters and 677 reflexions. The positions of the H atoms were determined from a difference map.

The value for *g* was $14(1) \times 10^{-7}$ with \bar{l} assumed to be unity; the minimum value of $F_o/F_o(\text{corr.})$ was 0.69. Atomic coordinates are listed in Table 1.†

The thermal motion of the atoms was analysed assuming that the molecule could be treated as a rigid body (Schomaker & Trueblood, 1968). The value of *L*

† Lists of thermal parameters (U_{ij} and *T*, *L*, and *S*), structure factors, short intermolecular contacts, bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35211 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$ for C and N, $\times 10^3$ for H), and deviations, Δ , from planarity (in Å $\times 10^{-3}$)

Isotropic thermal parameters (in Å² $\times 10^{-3}$) are calculated from the U_{ij} for non-hydrogen atoms. E.s.d.'s for the deviations from planarity are 0.006 for N, 0.007–0.009 for C, 0.013 for methyl C, 0.06 for H and 0.10 Å for methyl H atoms.

	<i>x</i>	<i>y</i>	<i>z</i>	Δ	U_{iso}
N(1)	1219 (4)	5203 (13)	-1301 (3)	15	50
N(2)	830 (4)	3589 (13)	-811 (5)	-7	49
N(3)	1142 (4)	2433 (13)	52 (4)	-18	51
C(1)	2148 (4)	5803 (14)	-812 (5)	20	43
C(2)	2637 (6)	7408 (17)	-1251 (6)	15	53
C(3)	3563 (6)	7912 (19)	-755 (7)	-6	62
C(4)	4012 (6)	6903 (18)	147 (7)	-18	61
C(5)	3537 (5)	5244 (15)	627 (5)	-12	48
C(6)	3912 (6)	4080 (18)	1572 (6)	-9	58
C(7)	3389 (6)	2505 (19)	1977 (6)	4	62
C(8)	2462 (6)	1993 (17)	1482 (6)	23	57
C(9)	2064 (5)	3048 (14)	559 (5)	9	42
C(10)	2592 (4)	4691 (13)	130 (5)	2	41
C(11)	-161 (7)	2928 (33)	-1328 (9)	-18	72
H(2)	234 (4)	818 (12)	-189 (4)	33	43 (18)
H(3)	389 (4)	900 (13)	-106 (4)	-15	51 (19)
H(4)	467 (5)	722 (16)	48 (5)	-60	87 (26)
H(6)	452 (4)	442 (13)	190 (4)	-22	60 (22)
H(7)	370 (4)	168 (11)	262 (4)	-39	40 (17)
H(8)	211 (4)	91 (15)	180 (4)	52	70 (24)
H(111)	-41 (7)	487 (27)	-156 (8)	655	132 (59)
H(112)	-35 (5)	116 (20)	-106 (6)	-347	122 (37)
H(113)	-18 (6)	213 (21)	-184 (6)	-625	102 (44)

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was used to correct the bond lengths for thermal motion. The average correction was 0.006 Å.

Bond distances corrected for thermal motion and angles are shown in Fig. 1.

Programs used were: data reduction (Kryger, 1975); averaging of symmetry-related reflexions, *DSORTH*, State University of New York at Buffalo; least-squares refinements, *KONSLS* (Pawley, 1971), and *LINUS* (Coppens & Hamilton, 1970); distances and angles, *ORFFE* (Busing, Martin & Levy, 1964); drawings, *ORTEP* (Johnson, 1965). Scattering factors were those of Cromer & Mann (1968) for C and N, and those of Stewart, Davidson & Simpson (1965) for H.

Discussion. The molecule has *mm*2 symmetry except for the methyl group which is rotated by 29° about the C–N bond. The packing is shown in Fig. 2. The approximate π -bond orders in (I), (III) (4,5-dianilino-2-phenyl-2H-1,2,3-triazole; Harlow, Brown, Dewar &

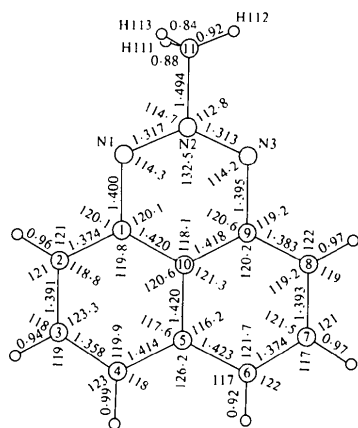


Fig. 1. Bond lengths (Å), corrected for thermal vibration, and angles (°). Standard deviations are: N–N, C–N = 0.007, C–C = 0.009, CH₃–C = 0.011, C–H = 0.05–0.10 Å; angles NNN ~ CNN ~ CCC = 0.7, CCH = 4, NCH = 6, HCH = 8°. The angles not shown on the figure are: N(2)–C(11)–H(111) = 107, N(2)–C(11)–H(112) = 111, N(2)–C(11)–H(113) = 102, H(111)–C(11)–H(112) = 132, H(111)–C(11)–H(113) = 96, H(112)–C(11)–H(113) = 104°.

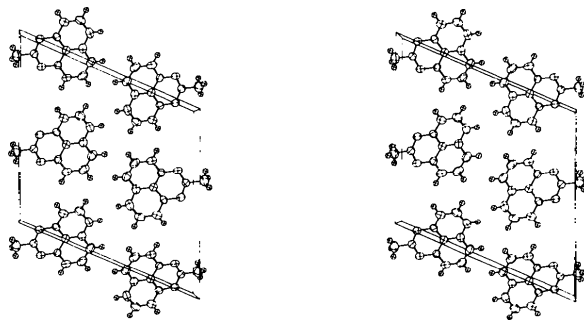


Fig. 2. The unit cell viewed down *b*; *a* is across the page, *c* up the page.

Table 2. Mean bond lengths (Å) compared with those in naphthalene

	(I)	Neutron ^a	X-ray ^b
<i>a</i>	1.379 (6)	1.373 (3)	1.377 (2)
<i>b</i>	1.392 (7)	1.410 (3)	1.411 (2)
<i>c</i>	1.366 (7)	1.373 (3)	1.377 (2)
<i>d</i>	1.419 (7)	1.423 (3)	1.424 (2)
<i>e</i>	1.420 (8)	1.420 (3)	1.421 (2)
<i>f</i>	1.419 (6)	1.423 (3)	1.424 (2)

(a) Hazell (1979); a new refinement with the data of Pawley & Yeats (1969). (b) Ponomarev, Filipenko & Atovmyan (1976).

Simonsen, 1977) and (IV) [4,5,6-tris(*p*-methoxyphenyl)-1,2,3-triazine; Oeser & Schiele, 1972] are for C–N: 0, 1, and $\frac{1}{2}$, and for N–N: $\frac{1}{2}$, 1, $\frac{1}{2}$. The mean bond distances are, for C–N: 1.397 (6), 1.335 (2), 1.366 (5) Å, and for N–N: 1.315 (6), 1.346 (2), and 1.316 (5) Å. Bartetzko & Gleiter (1978) have shown that the photoelectron spectra of (I) and of (II) (naphtho[1,8-*cd*]1,2,6thiadiazine) are almost identical, from which they infer a similarity in the chemical bonding and that 3*d* orbitals are unnecessary for the explanation of the bonding in (II). The angle C(4)–C(5)–C(6) = 126.2 (8)° is much larger than that expected (121.5°; Hazell, 1978) from the strain at angle *fg*. Comparison with naphthalene, Table 2, shows *b* and *c* to be short. Shortening *b* and *c* pulls C(4) and C(6) apart increasing the angle *dd*.

We thank Professor R. Gleiter for suggesting the problem and for providing the crystals. One of us (RM) is indebted to the Danish International Development Agency for financial aid, and the Facultad de Química (Uruguay) for leave of absence.

Note added in proof: After submitting this paper for publication we learnt that Gieren & Lamm (1980) (following paper) had also determined the structure. The results of the two determinations, referred to as **H** and **G**, are compared below. Cell dimensions, coordinates, and U_{ij} for **G** have been transposed to $P2_1/c$.

	H	G
<i>a</i>	15.916 (11) Å	15.929 (14) Å
<i>b</i>	3.955 (2)	3.955 (2)
<i>c</i>	15.372 (8)	15.385 (7)
β	112.83 (3)°	112.76 (5)°
Reflexions	677 ($I > 3\sigma$)	1070 ($I > 2\sigma$)
Variables	164	175
<i>R</i>	0.057	0.065
$\langle \sigma(\text{C,N-coord.}) \rangle$	0.008 Å	0.005 Å
$\langle \sigma(\text{H-coord.}) \rangle$	0.07 Å	0.07 Å
$\langle \sigma(U_{ij}) \rangle$	0.0045 Å ²	0.0027 Å ²

Half-normal probability plots (Abrahams & Keve, 1971) had the following gradients: coordinates (N, C,

and H) 1.02; U_{ij} (C and N) 1.12; bond lengths (not involving H) 1.18; angles (not involving H) 0.80. **G** finds the methyl group to be disordered with occupation factors of 0.6 and 0.4. The methyl hydrogens found by **H** are those for which **G** finds the highest occupation factor. A difference map with structure factors from **H**'s final refinement showed peaks close to the positions of H(77) and H(88) but none corresponding to H(99).

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The Structure of 2-Methyl-2H-naphtho[1,8-*de*]triazine

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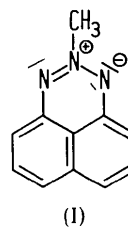
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Abstract. $C_{11}H_9N_3$, $M_r = 183.2$, monoclinic, space group $P2_1/a$, $a = 15.385$ (7), $b = 17.344$ (13), $c = 3.955$ (2) Å, $\gamma = 122.12$ (3)°, $Z = 4$, $D_o = 1.35$, $D_x = 1.36$ Mg m⁻³, μ (Cu $K\alpha$) = 0.689 mm⁻¹. Refinement with 1690 independent reflexions yielded an R of 0.065 for 1070 observed reflexions ($I > 2\sigma_I$). The molecule shows $mm2$ symmetry. The CH₃ group is disordered by rotation about the C–N bond resulting in two statistically occupied positions of the H atoms. In this way the disordered CH₃ group also fulfils approximately the $mm2$ symmetry. Bond lengths and angles are in agreement with those given by Hazell & Mariezcurrena [*Acta Cryst.* (1980). **B36**, 3140–3142].

Introduction. To compare the structures of sulfur-diimides with molecules containing the zwitterionic N_3R moiety, which is isoelectronic with the SN_2 unit, we have, among other structures (Gieren, Lamm, Haddon, Kaplan, Perkins & Flowerday, 1980), carried out an X-ray analysis of the title compound (I) (Perkins, 1964). When our analysis was finished we

heard from A. Hazell and R. Mariezcurrena, that they had also solved the structure of (I) (Hazell & Mariezcurrena, 1980).



(I) crystallizes from light petroleum in the form of blue-black elongated plates in the monoclinic space group $P2_1/a$. The crystal was 0.10 × 0.03 × 0.85 mm. To determine the lattice constants and for data collection a punch-tape-controlled diffractometer (Siemens AED) was used. Transformation into the space group $P2_1/c$ gives the lattice constants $a = 15.929$ (14), $b = 3.955$ (2), $c = 15.385$ (7) Å, $\beta = 112.76$ (5)°. These values are within the limits of error