

Table 2. *Interatomic distances (Å) and bond angles (°)*

C1—C2	1.395 (3)	C11—C21	1.387 (4)
C1—C6	1.401 (3)	C11—C7	1.492 (4)
C1—C7	1.493 (4)	C11—C61	1.392 (4)
C2—C3	1.382 (4)	C21—C31	1.384 (4)
C3—C4	1.384 (3)	C31—C41	1.379 (4)
C4—C5	1.389 (3)	C41—C51	1.379 (4)
C4—C8	1.507 (2)	C51—C61	1.379 (5)
C5—C6	1.378 (4)	C41—C81	1.502 (2)
C7—O7	1.220 (4)		
C2—C1—C7	123.0 (2)	C11—C7—O7	119.7 (2)
C2—C1—C6	118.3 (2)	C7—C11—C61	118.3 (2)
C6—C1—C7	118.7 (2)	C21—C11—C61	118.6 (3)
C1—C2—C3	120.0 (2)	C21—C11—C7	123.0 (2)
C2—C3—C4	121.7 (2)	C11—C21—C31	120.3 (2)
C3—C4—C5	118.2 (2)	C21—C31—C41	121.1 (2)
C3—C4—C8	121.2 (2)	C31—C41—C81	120.3 (2)
C5—C4—C8	120.6 (2)	C51—C41—C81	121.2 (2)
C4—C5—C6	120.9 (2)	C51—C41—C31	118.4 (3)
C1—C6—C5	120.8 (2)	C41—C51—C61	121.3 (2)
C1—C7—O7	119.4 (2)	C11—C61—C51	120.3 (2)
C1—C7—C11	120.9 (2)		

analysis of molecular geometry (Nardelli, 1983) at the University Computing Centre in Zagreb.

**Discussion.** The molecule with atom numbering is shown in the packing diagram (Fig. 1). Table 2 lists the bond lengths and angles.

The molecular geometry does not deviate from the geometry expected from standard atom types and hybridization (Table 2). Various symmetrically disubstituted aryl ketones, the title compound, and benzophenone by itself are not planar molecules. The ring twisting influences the delocalization of the  $\pi^*$  electrons and can explain the changes of optical properties of benzophenones in relation to the electronic properties of the substituents (Batley, Bramley & Robinson, 1979).

The torsion angle about the bond connecting the phenyl ring and keto group is  $26.0^\circ$  in benzophenone (Fleischer, Sung & Hawkinson, 1968),  $27.9^\circ$  in 4,4'-

dichlorobenzophenone (Shields & Kennard, 1977),  $25.2^\circ$  in 4,4'-diiodobenzophenone (van der Velden & Noordik, 1979),  $24$  and  $33^\circ$  in 4,4'-diaminobenzophenone (van der Velden & Noordik, 1980), and  $22.6(4)$  ( $C6-C1-C7-O7$ ) and  $32.2(4)^\circ$  ( $C61-C11-C7-O7$ ) in the present structure. The 4,4'-halogen substituted molecules exhibit a crystallographic twofold axis. Molecular packing is realized *via* van der Waals interactions (Fig. 1).

Support of this research by the Self-Management Council for Scientific Research of SR Croatia is gratefully acknowledged. The crystals used in this structure determination were prepared by Mr Sc. V. Volovšek, Ruđer Bošković Institute.

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*Acta Cryst.* (1990). **C46**, 432–435

## Structure of Diethyl 1-(8-Dimethylamino-1-naphthyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate

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(Received 15 February 1989; accepted 14 June 1989)

**Abstract.**  $C_{20}H_{22}N_4O_4$ ,  $M_r = 382.42$ , monoclinic,  $P2_1/n$ ,  $a = 9.498(1)$ ,  $b = 22.241(1)$ ,  $c = 9.589(1)$  Å,  $\beta = 97.47(1)^\circ$ ,  $V = 2008.4(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.27$ ,  $D_x = 1.265$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu =$

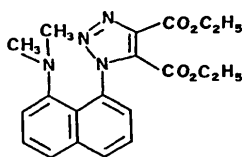
$0.0971$  mm<sup>-1</sup>,  $F(000) = 808$ ,  $T = 295$  K,  $R = 0.049$  for 2487 observed independent reflections. The dihedral angle between the mean plane of the naphthalene ring and that of the triazole ring in the title

0108-2701/90/030432-04\$03.00

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compound is  $53.5(1)^\circ$ . The naphthalene framework is very distorted because of the repulsion between the triazole ring and the dimethylamino group.

**Introduction.** Naphthalenes with substituents in 1 and 8 positions, so called *peri*-substituted naphthalenes, exhibit unique properties in both structure and reactivity, because the substituents exist in close proximity. The typical example is the unusual basicity of 1,8-bis(dimethylamino)naphthalene (Alder, Bowman, Steele & Winterman, 1968), the reason for which is probably the existence of the two neighboring dimethylamino groups. Recently, we have synthesized novel 1,8-diheteroaromatic naphthalenes, 1,1'-(1,8-naphthylene)di-1*H*-1,2,3-triazoles, and investigated their spectroscopic properties (Honda, Nakanishi, Nagawa & Yabe, 1984). In connection with these studies, we have prepared the title compound and found that the rotation of the C—N bond between the dimethylamino group and the naphthalene ring is restricted at room temperature by NMR spectroscopy (Nagawa, Honda & Nakanishi, 1987). This result suggests that the compound has a very overcrowded structure at the *peri* positions. In this paper, we describe the crystal and molecular structure in comparison with that of other *peri*-substituted naphthalenes.



(I)

**Experimental.** Title compound was synthesized by the method previously reported (Nagawa, Honda & Nakanishi, 1987); plate-shaped colorless crystals (m.p. 354 K) obtained by slow evaporation of a hexane solution. Crystal  $0.50 \times 0.35 \times 0.10$  mm.  $D_m$  measured by flotation. Data collection: Rigaku AFC-4 four-circle diffractometer, graphite-monochromated Mo  $K\alpha$  radiation; cell parameters determined by least squares from  $2\theta$  values for 25 reflections ( $20 < 2\theta < 30^\circ$ ); systematic absences of  $h0l$  for  $h + l = 2n$ ,  $0k0$  for  $k = 2n$ ; intensity data  $2 < 2\theta < 55^\circ$ ,  $\omega$ - $2\theta$  scan,  $-12 \leq h \leq 12$ ,  $0 \leq k \leq 28$ ,  $0 \leq l \leq 12$ , scan speed  $2^\circ \text{ min}^{-1}$ ; three standard reflections (320, 031, and 121) showed only statistical variations within  $\pm 1\%$ ; 5074 (including systematically absent) reflections collected, 2487 with  $|F_o| > 3\sigma(|F_o|)$  used. No correction for absorption. Structure solved by direct methods using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). *E* map using  $212 |E| > 1.2$  revealed positions of all non-H atoms. H atoms placed at idealized positions.

Full-matrix least-squares refinement (on *F*) using scattering factors from *International Tables for X-ray Crystallography* (1974), anisotropic temperature factors for non-H atoms, isotropic for H,  $R = 0.049$  and  $wR = 0.045$ ;  $w = 1/(a|F_o|^2 + b|F_o| + c)$ ;  $a = 0.0024$ ,  $b = -0.0591$ ,  $c = 0.703$ ;  $S = 1.06$ . Max. and min. heights in final difference map  $\pm 0.2 e \text{ \AA}^{-3}$ . Max.  $\Delta/\sigma = 0.076$  [*z* of O(2)]. Calculations carried out on a FACOM M-780 with *UNICSIII* (Sakurai & Kobayashi, 1979).

**Discussion.** Final atomic positions and equivalent isotropic thermal parameters are given in Table 1.\* An *ORTEP* (Johnson, 1965) drawing of the molecule with the numbering of atoms is shown in Fig. 1. Bond lengths and angles are given in Table 2.

The deviations of each atom of the triazole ring from the mean plane are within  $0.01 \text{ \AA}$ , which suggests that the ring is almost planar due to an aromatic ring system. The dihedral angle between the mean plane of the triazole ring and that of the naphthalene ring is  $53.5(1)^\circ$ . The torsion angle C(9)—C(1)—N(1)—N(2),  $-128.9(3)^\circ$ , shows that N(2) is much closer to the C(2)—C(3) axis than to the C(9)—C(10) axis. The direction of the triazole ring is opposite to that in the case of 1,1'-(1,8-naphthylene)-

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and details of least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52348 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

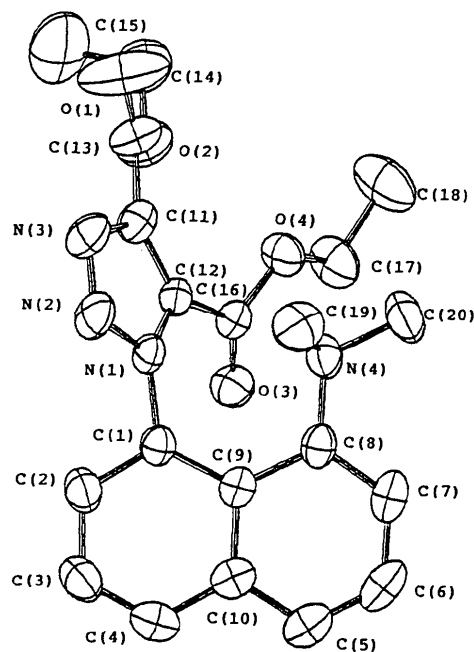


Fig. 1. A perspective view of the molecule, with the numbering scheme.

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
C(1)	3666 (3)	1770 (1)	4973 (3)	3.6 (1)
C(2)	4490 (3)	2197 (1)	5710 (3)	4.7 (1)
C(3)	3928 (4)	2582 (2)	6633 (4)	5.8 (1)
C(4)	2532 (4)	2554 (2)	6741 (4)	5.7 (1)
C(5)	162 (4)	2134 (2)	6070 (4)	5.6 (1)
C(6)	-712 (3)	1740 (2)	5345 (4)	5.9 (1)
C(7)	-171 (3)	1283 (2)	4558 (3)	4.8 (1)
C(8)	1264 (3)	1238 (1)	4464 (3)	3.8 (1)
C(9)	2199 (3)	1694 (1)	5112 (3)	3.5 (1)
C(10)	1629 (3)	2130 (1)	5979 (3)	4.5 (1)
C(11)	5383 (3)	990 (1)	2386 (3)	4.3 (1)
C(12)	4215 (2)	1311 (1)	2662 (3)	3.5 (1)
C(13)	5865 (3)	788 (2)	1040 (4)	5.9 (1)
C(14)	5834 (6)	1013 (3)	-1392 (5)	8.7 (2)
C(15)	7132 (8)	1324 (6)	-1567 (7)	12.2 (3)
C(16)	2961 (3)	1543 (1)	1721 (3)	3.6 (1)
C(17)	1534 (5)	1365 (2)	-447 (4)	6.1 (1)
C(18)	1297 (7)	867 (3)	-1453 (5)	8.6 (2)
C(19)	2699 (5)	341 (2)	4660 (5)	6.2 (1)
C(20)	801 (5)	435 (3)	2732 (5)	7.3 (1)
N(1)	4421 (2)	1410 (1)	4059 (2)	3.6 (1)
N(2)	5667 (2)	1155 (1)	4635 (3)	5.1 (1)
N(3)	6241 (2)	904 (1)	3615 (3)	5.3 (1)
N(4)	1830 (2)	762 (1)	3742 (2)	4.5 (1)
O(1)	6597 (4)	365 (2)	974 (4)	12.3 (1)
O(2)	5423 (3)	1150 (1)	-5 (2)	6.6 (1)
O(3)	2401 (2)	2012 (1)	1886 (2)	4.6 (1)
O(4)	2610 (2)	1160 (1)	685 (2)	4.7 (1)

Table 2. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) in (I) with *e.s.d.*'s in parentheses

C(1)—C(2)	1.368 (4)	C(1)—C(9)	1.427 (3)
C(1)—N(1)	1.444 (3)	C(2)—C(3)	1.386 (5)
C(3)—C(4)	1.345 (5)	C(4)—C(10)	1.412 (4)
C(5)—C(6)	1.338 (5)	C(5)—C(10)	1.407 (5)
C(6)—C(7)	1.402 (5)	C(7)—C(8)	1.381 (4)
C(8)—C(9)	1.436 (3)	C(8)—N(4)	1.410 (4)
C(9)—C(10)	1.429 (4)	C(11)—C(12)	1.374 (4)
C(11)—C(13)	1.493 (5)	C(11)—N(3)	1.356 (4)
C(12)—C(16)	1.490 (3)	C(12)—N(1)	1.346 (3)
C(13)—O(1)	1.177 (5)	C(13)—O(2)	1.311 (4)
C(16)—O(3)	1.192 (3)	C(16)—O(4)	1.318 (3)
C(19)—N(4)	1.464 (5)	C(20)—N(4)	1.475 (5)
N(1)—N(2)	1.363 (3)	N(2)—N(3)	1.305 (4)
C(2)—C(1)—C(9)	122.2 (3)	C(2)—C(1)—N(1)	113.8 (2)
C(9)—C(1)—N(1)	124.0 (2)	C(1)—C(2)—C(3)	121.1 (3)
C(2)—C(3)—C(4)	119.1 (3)	C(3)—C(4)—C(10)	122.0 (3)
C(6)—C(5)—C(10)	121.1 (3)	C(5)—C(6)—C(7)	120.6 (3)
C(6)—C(7)—C(8)	121.4 (3)	C(7)—C(8)—C(9)	118.7 (3)
C(7)—C(8)—N(4)	122.0 (2)	C(9)—C(8)—N(4)	119.3 (2)
C(1)—C(9)—C(8)	126.9 (2)	C(1)—C(9)—C(10)	115.0 (2)
C(8)—C(9)—C(10)	118.1 (2)	C(4)—C(10)—C(5)	120.2 (3)
C(4)—C(10)—C(9)	120.2 (3)	C(5)—C(10)—C(9)	119.6 (3)
C(12)—C(11)—C(13)	132.0 (3)	C(12)—C(11)—N(3)	108.3 (2)
C(13)—C(11)—N(3)	119.5 (3)	C(11)—C(12)—C(16)	131.7 (2)
C(11)—C(12)—N(1)	105.1 (2)	C(16)—C(12)—N(1)	123.2 (2)
C(11)—C(13)—O(1)	122.5 (3)	C(11)—C(13)—O(2)	111.9 (3)
O(1)—C(13)—O(2)	125.6 (4)	C(15)—C(14)—O(2)	109.8 (5)
C(12)—C(16)—O(3)	123.9 (2)	C(12)—C(16)—O(4)	109.7 (2)
O(3)—C(16)—O(4)	126.4 (2)	C(18)—C(17)—O(4)	106.5 (3)
C(1)—N(1)—N(2)	117.3 (2)	C(1)—N(1)—C(12)	132.5 (2)
C(12)—N(1)—N(2)	109.9 (2)	N(1)—N(2)—N(3)	107.4 (2)
C(11)—N(3)—N(2)	109.2 (2)	C(8)—N(4)—C(19)	114.0 (3)
C(8)—N(4)—C(20)	115.5 (3)	C(13)—O(2)—C(14)	118.0 (4)
C(16)—O(4)—C(17)	116.2 (2)		

di-1*H*-1,2,3-triazole (Nagawa, Goto, Honda & Nakanishi, 1986).

The plane containing C(8), N(4), and C(19) is almost parallel to the triazole ring and the direction of N(4)—C(19) is opposite to the 5-ethoxycarbonyl group attached to C(12). On the other hand, the plane containing C(8), N(4), and C(20) is almost parallel to the naphthalene ring, since the torsion angle C(7)—C(8)—N(4)—C(20) is 18.9 (4) $^\circ$ . Such a conformation of the dimethylamino group is similar to that of the dimethylamino groups in the crystal structure of 1,8-bis(dimethylamino)naphthalene (Einspahr, Robert, Marsh & Roberts, 1973). The environments of the two *N*-methyl groups in the title compound are very different to each other. In fact, the two *N*-methyl groups in the title compound show very different  $^1\text{H}$  NMR chemical shifts at 2.08 and 2.53 p.p.m. from Me<sub>4</sub>Si in CDCl<sub>3</sub> solution (Nagawa, Honda & Nakanishi, 1987).

The fusion angle C(1)—C(9)—C(8), 126.9 (2) $^\circ$ , is distinctly large compared with that of 1-(1-naphthyl)-1*H*-1,2,3-triazole, 123.7 $^\circ$  (Nagawa, Goto, Honda & Nakanishi, 1987). The repulsion between the triazole ring and the dimethylamino group causes this enlargement of the angle. The angle C(9)—C(1)—N(1), 124.0 (2) $^\circ$ , shows that the C(1)—N(1) axis inclines toward the C(2)—C(3) axis. Such distortion is observed in several 1,8-disubstituted naphthalenes, and the enlargement of the angle is also due to the steric overcrowding.

The distance of C(8)—N(4), 1.410 (4)  $\text{\AA}$ , is shorter than that of C(1)—N(1), 1.444 (3)  $\text{\AA}$ , which suggests that the former bond has partial double-bond character. However, the bond between the dimethylamino group and the naphthalene ring in the title

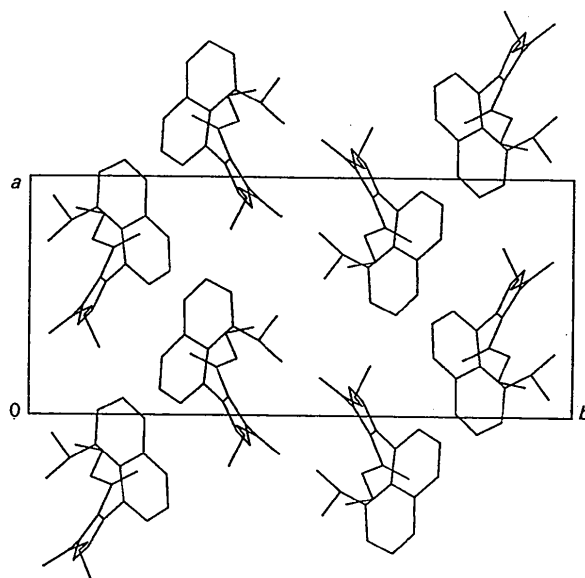


Fig. 2. Packing of molecules in the unit cell (viewed down *c*).

compound is long compared with that in 1-dimethylamino-4-nitrobenzene, 1.358 Å (Mak & Trotter, 1965) and in *p*-dimethylaminobenzaldehyde oxime, 1.380 Å (Bachechi & Zambonelli, 1972). Therefore, the degree of the double-bond character in the title compound is relatively small.

The torsion angles C(12)—C(11)—C(13)—O(1),  $-154.2(4)^\circ$ , and C(11)—C(12)—C(16)—O(3),  $-142.9(3)^\circ$ , show that the two carbonyl groups twist from the mean plane of the triazole ring on opposite sides. These directions differ notably in the case of diisopropyl 1-(1-naphthyl)-1*H*-1,2,3-triazole-4,5-dicarboxylate (Nagawa, Goto, Honda & Nakanishi, 1988), in which the carbonyl group at the 4-position exists in the triazole plane and at the 5-position it twists from the triazole plane. The results reflect the requirements of intramolecular contacts of the extra dimethylamino group. The larger temperature factors of C(15) and O(1) atoms might be due to the disorder.

The packing of the molecule in the crystal is shown in Fig. 2. The crystal structure is stabilized mainly by van der Waals forces; the shortest intermolecular distance is 3.315(5) Å for C(19)(*x*, *y*, *z*)...N(3)(1 - *x*, -*y*, 1 - *z*).

*Acta Cryst.* (1990). **C46**, 435–437

## Structure of 3-(1-Pyridinio)indole-2-thiolate

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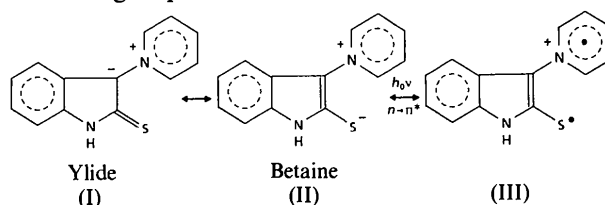
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(Received 13 February 1989; accepted 10 May 1989)

**Abstract.** C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>S, *M<sub>r</sub>* = 226.3, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.037(4), *b* = 8.076(3), *c* = 14.124(4) Å, β = 104.59(3)°, *V* = 1107.9(6) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.34(1), *D<sub>x</sub>* = 1.36 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 2.6 cm<sup>-1</sup>, *F*(000) = 472, *T* = 295 K, *R* = 0.039 for 2057 observed reflexions. Sulfur forms a hydrogen bond to the NH group of the neighbouring molecule symmetrically related by the screw axis along *b*. The phenyl ring is rotated out of the indolyl plane by 57°.

**Introduction.** X-ray structure analysis of the title compound has been used to confirm the chemical constitution of the product of a new synthetic method for the preparation of indolyl-based com-

pounds (Gonda, Kristian & Imrich, 1987; Gonda & Kristian, 1988) and to obtain information about the contributions of the resonance states (I)–(III) to the average crystal structure. This paper is part of a general project on the development of biologically efficient indolyl compounds substituted by different function groups.



0108-2701/90/030435-03\$03.00

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