

bond involving H(7) with the carbonyl oxygen or intermolecular association with a *p*-nitro group. We ascribe this, as before, to the steric constraints of the *o*-nitro group and the methyl group at C(20) which largely surround the hydrogen on N(7).

(2) is centrosymmetric and exhibits the *E,E* conformation. This structure can be compared with that of (6) whose structure was determined with two molecules of DMF (Willey & Drew, 1983). The solvent was hydrogen bonded to the two H(7) atoms in the dimer. In (2) the *o*-nitro group and the methyl group at C(10) effectively shield the H(7) atom from solvent participation in a hydrogen bond. H(7) atoms are hydrogen bonded to the *o*-nitro group at O(1).

The individual dimensions in (1), (2) and (3) follow the pattern established in previous structures in that the dimensions of the phenylhydrazone skeleton are very dependent upon the presence of intramolecular hydrogen bonding between carbonyl oxygen and N(7). Thus with such a bond, the C(4)–N(7), N(7)–N(8), and N(8)–C(9) bond lengths are 1.400, 1.307, 1.313 Å and without such a bond 1.36, 1.39, 1.28 Å. (These are average values from 18 and nine structures respectively, Willey & Drew, 1983, and references therein.) Present dimensions are in (1) 1.363 (7), 1.334 (5), 1.278 (6) Å; in (2) 1.324 (13), 1.368 (13), 1.282 (12) Å and in (3) 1.370 (4), 1.362 (4) and 1.308 (4) Å so they fit in well with the pattern.

Least-squares-planes' calculations show that the molecules are slightly distorted from planarity. The *o*-nitro groups are twisted by angles of 12.1 (1), 5.4 (1), 1.6 (1)° from the plane of the benzene ring. In (3) the *p*-nitro group is twisted by 2.6 (1)°. The angle between the plane of atoms C(9), C(10) and C(20) and the benzene ring is an indication of the steric strain between the methyl group at C(10) and the N(7) hydrogen atom. In the three structures this angle is 6.3 (1),

5.6 (1), 5.0 (1)°, respectively, showing that the repulsions between the C(10) methyl group and H(7) are of minor import, though it is clear from the figures that the arrangement of the hydrogen atoms at C(10) is such as to maximize such contacts.

In the three structures there are no intermolecular contacts less than the sum of van der Waals radii.

We thank Haydn Beaton for his assistance with the preparative work, A. W. Johans for his help with the crystallographic investigations and SERC for funds for the diffractometer.

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Structure of (*E*)-4,4-Dimethyl-1-(1-naphthyl)-1-(1*H*-1,2,4-triazol-1-yl)pent-1-en-3-one, C₁₉H₁₉N₃O

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(Received 25 July 1984; accepted 5 November 1984)

Abstract. $M_r = 305.4$, $P2_1/c$, $a = 18.971$ (7), $b = 3354.4$ Å³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $Z = 8$ (two independent molecules per asymmetric unit), $D_m = 1.20$ (2), $D_x = 1.21$ g cm⁻³, $\mu = 0.83$ cm⁻¹, $F(000) = 1296$, room temperature, final $R = 0.0847$ for 1268

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reflections classed as observed. The α,β -unsaturated carbonyl function is nearly planar and adopts a *cis* conformation. The naphthyl ring is twisted by 75.8 (10) and 72.7 (10)°, respectively, in the two molecules, out of the plane containing the C—C double bond while the triazolyl ring, which shows significant delocalization, lies almost in that plane. This conformation allows extensive conjugation between the α,β -unsaturated ketone and the heterocyclic group. The exocyclic angles of the triazolyl ring are very asymmetric with C—N—C [129 (1), 130 (1)°] significantly larger than C—N—N [119 (1), 122 (1)°].

Introduction. The class of γ -ketotriazoles, of which the title compound is an example (Balasubramanyan & Lewis, 1976), was discovered during the investigation of the biological activity of compounds related to the well established systemic fungicide triadimefon (Martin & Morris, 1979). The γ -ketotriazoles have no fungicidal activity but are good pre-emergence herbicides. The exact mode of action is unknown, but the compounds are slow-acting and inhibit root and shoot growth. The *E* isomers are more active than the corresponding *Z* isomers and structure–activity relationships indicate that the triazole group and orientation of the aromatic ring play important roles (Anderson, Heritage & Branch, 1983). Thus, we have determined the crystal structure of the title compound to establish its solid-state conformation as part of a programme to study the relationship between conformation and biological activity in this series of herbicides.

Experimental. Recrystallization from ethanol:water (1:1); D_m by flotation in benzene:carbon tetrachloride; crystal, yellow hexagonal prism, approximate dimensions 0.28 × 0.36 × 0.06 mm; Enraf–Nonius CAD-4 four-circle diffractometer; cell dimensions refined from settings of 25 reflections having $\theta = 8.0$ to 10.0°; Lorentz, polarization but no absorption corrections applied; two standard reflections ($\bar{3}12$, 112) monitored throughout, intensity variation <4%; 3487 reflections measured up to $\theta = 20^\circ$ using $\omega - \frac{4}{3}\theta$ scans, variable scan speed; index ranges $h = -18$ to 17, $k = 0$ to 16, $l = 0$ to 10; 3126 independent reflections, R_{int} 0.037, 1268 with $I \geq 1.0\sigma(I)$ considered observed; structure solved by multiresolution direct methods for two independent molecules (I and II); blocked full-matrix least-squares refinement minimizing $\sum w(F_o - F_c)^2$ with $w = 1.1899/[\sigma^2(F_o) + 0.0001(F_o)^2]$ of atomic coordinates and anisotropic temperature factors for all non-H atoms, and isotropic temperature factors for all H atoms; H atoms included in positions calculated from geometry of molecule (C—H = 1.08 Å); final $R = 0.0847$, $wR = 0.0546$; max. $\Delta/\sigma = 0.65$; min. $\Delta\rho = -0.29$, max. $\Delta\rho = 0.27 e \text{ \AA}^{-3}$; no correction for secondary extinction; scattering factors calculated from an analytical approximation (*International Tables for*

X-ray Crystallography, 1974); computer programs, *SHELX* (Sheldrick, 1976) and *PLUTO* (Motherwell & Clegg, 1978). A final value of $U = 0.079$ (32) Å² was refined for H(5) while the common isotropic temperature factors applied to the methyl, naphthyl and triazolyl H atoms refined to final values of $U = 0.135$ (14), 0.165 (20) and 0.210 (56) Å² respectively.

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1;* bond lengths and angles in Table 2 and the atomic numbering scheme in Fig. 1. The two independent molecules adopt similar conformations such that the carbonyl group and the unsaturated bond C(4)=C(5) are *cis* orientated and nearly coplanar (Fig. 1). The dihedral angle between the two groups [as defined by the planes containing atoms C(5), C(6), O(1), C(71) and N(1), C(31), C(4), C(5), C(6)] is 30.9 (10) (I) and 28.1 (10)° (II). This arrangement avoids steric interactions between the butyl and naphthyl groups. The triazolyl ring, which is planar, is orientated such that N(2) is directed towards H(5) thus allowing the ring to lie almost in the plane containing atoms N(1), C(4), C(5), C(6) and C(31). The dihedral angle† between the latter plane and the triazolyl ring is 7.4 (I) and 13.0° (II) and hence could facilitate conjugation between the α,β -unsaturated ketone function and the triazolyl ring, although this is not reflected by significant shortening of the single bonds N(1)—C(4) and C(5)—C(6) or lengthening of the double bond C(4)—C(5). The orientation of the naphthyl ring, which is planar, appears to be governed by an attempt to minimize steric repulsion with (i) the carbonyl function and (ii) the triazolyl ring. The resulting dihedral angles between the naphthyl ring and other parts of the molecule are as follows: (i) with the plane containing atoms N(1), C(31), C(4), C(5) and C(6), 75.8 (I) and 72.7° (II); (ii) with the triazolyl ring, 78.8 (I) and 76.8° (II); (iii) with the plane containing atoms C(5), C(6), O(1) and C(71), 73.8 (I) and 71.6° (II). Steric repulsion between the naphthyl ring and carbonyl group may also be responsible for the unusually large angle C(5)—C(4)—C(31).

All four C—N distances in the triazolyl ring are shorter than the normal single bond as is the bond N(1)—N(2). The three atoms bonded to N(1) are coplanar with it and, taken together, these data indicate extensive delocalization in the heterocyclic ring. The most noteworthy feature of the triazolyl ring is the asymmetry of the exocyclic angles at N(1), C(4)—N(1)—C(1) being much larger than C(4)—N(1)—N(2).

* 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 39888 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† E.s.d.'s are 1.0° for dihedral angles.

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

B_{eq} values have been calculated by reference to Willis & Pryor (1975).

Molecule (I)	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{\AA}^2)$
N(1)	3677 (6)	3803 (6)	1814 (9)	4.5 (5)
N(2)	4030 (6)	3880 (6)	863 (12)	6.6 (6)
N(3)	2918 (6)	4490 (6)	382 (12)	7.7 (7)
O(1)	5028 (4)	2735 (4)	5168 (7)	5.3 (4)
C(1)	3034 (7)	4183 (8)	1536 (13)	7.2 (8)
C(2)	3543 (10)	4311 (9)	42 (13)	6.9 (9)
C(31)	3610 (6)	3404 (10)	3961 (10)	4.5 (7)
C(32)	3212 (8)	2748 (8)	4087 (11)	5.6 (7)
C(33)	2763 (6)	2746 (9)	4922 (17)	6.6 (9)
C(34)	2754 (7)	3407 (12)	5664 (13)	6.7 (9)
C(35)	3175 (7)	4083 (11)	5554 (12)	5.3 (8)
C(36)	3612 (6)	4107 (9)	4658 (10)	3.9 (7)
C(37)	4044 (6)	4795 (9)	4541 (10)	5.1 (7)
C(38)	3993 (6)	5441 (7)	5312 (14)	6.4 (7)
C(39)	3537 (11)	5407 (13)	6156 (16)	9.6 (13)
C(40)	3192 (10)	4778 (12)	6290 (18)	8.4 (12)
C(4)	4023 (6)	3369 (6)	2930 (10)	4.5 (6)
C(5)	4617 (7)	2931 (6)	2962 (10)	4.2 (6)
C(6)	5030 (5)	2511 (7)	4111 (11)	4.0 (6)
C(71)	5498 (6)	1786 (7)	3915 (11)	4.2 (6)
C(72)	5819 (6)	1389 (6)	5206 (10)	6.2 (7)
C(73)	6126 (5)	2075 (6)	3371 (10)	7.4 (7)
C(74)	5013 (6)	1180 (6)	3021 (9)	6.0 (7)
Molecule (II)				
N(1)	8646 (7)	1226 (6)	1845 (11)	6.0 (7)
N(2)	8956 (5)	1102 (6)	3101 (11)	5.7 (6)
N(3)	7849 (8)	501 (8)	2541 (16)	10.5 (9)
O(1)	9995 (4)	2267 (4)	-282 (7)	5.5 (4)
C(1)	8001 (10)	864 (11)	1537 (14)	9.5 (11)
C(2)	8461 (11)	688 (8)	3428 (15)	7.9 (10)
C(31)	8614 (5)	1569 (5)	-381 (10)	4.5 (6)
C(32)	8215 (6)	2187 (8)	-988 (12)	6.6 (7)
C(33)	7821 (9)	2140 (12)	-2302 (19)	9.8 (12)
C(34)	7873 (7)	1425 (10)	-2905 (16)	7.3 (10)
C(35)	8281 (7)	791 (9)	-2265 (14)	4.7 (8)
C(36)	8673 (7)	848 (7)	-928 (14)	4.9 (7)
C(37)	9080 (6)	195 (10)	-291 (11)	6.0 (7)
C(38)	9084 (6)	-499 (10)	-974 (16)	7.1 (9)
C(39)	8743 (9)	-547 (11)	-2225 (19)	8.5 (12)
C(40)	8354 (8)	49 (14)	-2896 (14)	8.6 (12)
C(4)	9022 (7)	1650 (8)	1054 (11)	4.8 (7)
C(5)	9563 (7)	2129 (7)	1531 (12)	5.4 (7)
C(6)	9984 (6)	2546 (7)	778 (12)	4.6 (7)
C(71)	10458 (6)	3247 (8)	1346 (11)	5.0 (7)
C(72)	10786 (6)	3621 (6)	353 (9)	7.1 (7)
C(73)	11053 (5)	2950 (6)	2470 (9)	5.6 (7)
C(74)	9969 (6)	3854 (6)	1786 (9)	6.1 (7)

We have observed a similar pattern in related triazole systems (Nowell, Walker & Anderson, 1982) and it appears to be a function of the heterocyclic ring itself rather than the influence of any intra- or intermolecular interactions. It is found, for example, that while other 1-substituted 1*H*-1,2,4-triazoles (*e.g.* Wooden, Hoskin & Olofson, 1981) and *N*-substituted pyrazoles (*e.g.* Sikirica & Vicković, 1980) show this asymmetry, *N*-substituted imidazoles (*e.g.* Peeters, Blaton & de Ranter, 1979) and 2-substituted 1,2,3-triazoles (Harlow, Brown, Dewar & Simonsen, 1977) do not.

We thank the SERC for an equipment grant and computing facilities (IWN), the SERC and Imperial Chemical Industries Limited for a CASE award (SKB), the ARC (D. Hughes, Rothamstead Experimental Research Station) for diffractometer facilities and N. H. Anderson (Long Ashton Research Station, formerly at ICI Plant Protection Division) for helpful discussions.

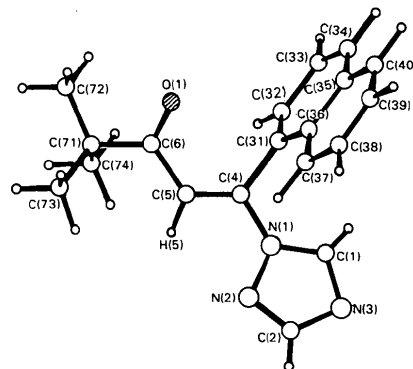


Fig. 1. The conformation of the title compound (molecule II). Molecule (I) has a very similar conformation.

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with *e.s.d.*'s in parentheses

	(I)	(II)		(I)	(II)		(I)	(II)
N(1)—N(2)	1.376 (18)	1.362 (16)	C(33)—C(34)	1.375 (25)	1.383 (27)	C(40)—C(35)	1.410 (26)	1.445 (27)
N(2)—C(2)	1.327 (18)	1.288 (23)	C(34)—C(35)	1.408 (25)	1.393 (21)	C(4)—C(5)	1.338 (17)	1.305 (17)
C(2)—N(3)	1.362 (23)	1.348 (21)	C(35)—C(36)	1.434 (20)	1.462 (20)	C(5)—C(6)	1.477 (15)	1.460 (19)
N(3)—C(1)	1.326 (19)	1.345 (25)	C(36)—C(31)	1.400 (20)	1.365 (16)	C(6)—O(1)	1.212 (15)	1.252 (15)
C(1)—N(1)	1.341 (17)	1.331 (22)	C(36)—C(37)	1.439 (20)	1.416 (19)	C(6)—C(71)	1.552 (17)	1.514 (17)
N(1)—C(4)	1.427 (14)	1.438 (19)	C(37)—C(38)	1.389 (20)	1.381 (23)	C(71)—C(72)	1.536 (15)	1.514 (17)
C(4)—C(31)	1.525 (18)	1.566 (15)	C(38)—C(39)	1.414 (26)	1.357 (25)	C(71)—C(73)	1.537 (17)	1.524 (14)
C(31)—C(32)	1.360 (21)	1.353 (15)	C(39)—C(40)	1.270 (30)	1.343 (27)	C(71)—C(74)	1.541 (15)	1.534 (17)
C(32)—C(33)	1.395 (23)	1.441 (22)						
C(1)—N(1)—N(2)	111.9 (10)	108.7 (12)	C(32)—C(31)—C(36)	123.4 (12)	124.2 (11)	C(38)—C(39)—C(40)	121.7 (19)	124.1 (18)
C(1)—N(1)—C(4)	129.1 (12)	129.6 (12)	C(31)—C(32)—C(33)	120.9 (13)	122.0 (13)	C(35)—C(40)—C(39)	124.1 (20)	119.1 (14)
N(2)—N(1)—C(4)	118.9 (10)	121.6 (11)	C(32)—C(33)—C(34)	118.8 (14)	116.0 (15)	C(4)—C(5)—C(6)	123.1 (11)	123.9 (12)
N(1)—N(2)—C(2)	99.8 (12)	101.6 (11)	C(33)—C(34)—C(35)	120.4 (14)	121.3 (15)	C(5)—C(6)—O(1)	121.9 (10)	118.6 (10)
N(2)—C(2)—N(3)	116.3 (14)	118.9 (15)	C(34)—C(35)—C(36)	121.3 (14)	121.9 (14)	C(5)—C(6)—C(71)	117.1 (10)	119.6 (11)
C(2)—N(3)—C(1)	103.0 (11)	98.9 (14)	C(34)—C(35)—C(40)	123.2 (15)	121.7 (14)	O(1)—C(6)—C(71)	120.9 (10)	121.4 (11)
N(3)—C(1)—N(1)	108.8 (13)	111.9 (13)	C(36)—C(35)—C(40)	115.5 (15)	116.4 (12)	C(6)—C(71)—C(72)	108.7 (10)	109.8 (10)
N(1)—C(4)—C(5)	120.3 (11)	121.7 (11)	C(31)—C(36)—C(35)	115.0 (13)	114.6 (11)	C(6)—C(71)—C(73)	109.4 (9)	108.5 (10)
N(1)—C(4)—C(31)	113.4 (10)	111.2 (10)	C(35)—C(36)—C(37)	121.5 (13)	121.0 (12)	C(6)—C(71)—C(74)	109.4 (9)	107.3 (9)
C(31)—C(4)—C(5)	126.0 (10)	126.3 (12)	C(31)—C(36)—C(37)	123.4 (12)	124.4 (12)	C(72)—C(71)—C(73)	108.9 (9)	110.9 (9)
C(4)—C(31)—C(32)	116.4 (12)	119.8 (10)	C(36)—C(37)—C(38)	116.4 (12)	117.6 (12)	C(72)—C(71)—C(74)	109.2 (9)	109.8 (10)
C(4)—C(31)—C(36)	120.0 (12)	116.0 (10)	C(37)—C(38)—C(39)	120.7 (14)	121.7 (14)	C(73)—C(71)—C(74)	111.2 (10)	110.4 (9)

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Acta Cryst. (1985). C41, 597–599

Captodative Substitution and Cyclopropane Geometry. III. Methyl 2-*tert*-Butylthio-1-*t*-chloro-2-*r*-cyano-1-cyclopropanecarboxylate, C₁₀H₁₄ClNO₂S

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(Received 12 September 1984; accepted 19 November 1984)

Abstract. $M_r = 247.75$, monoclinic, $P2_1/n$, $a = 8.953$ (2), $b = 23.338$ (8), $c = 6.041$ (2) Å, $\beta = 99.66$ (2)°, $V = 1244.3$ (6) Å³, $Z = 4$, $D_x = 1.32$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 4.54$ cm⁻¹, $F(000) = 520$, $T = 291$ K, $R = 0.044$ for 1313 observed reflections. The cyclopropyl ring bond lengths are significantly different: C(1)–C(2) = 1.545 (5), C(1)–C(3) = 1.477 (6) and C(2)–C(3) = 1.506 (5) Å. These variations resulted from the substituent effects; captodative substitution (here CN, *tert*-butylthio), as π -acceptor groups, shortens the distal bond and lengthens the vicinal bonds of the cyclopropyl ring.

Introduction. The crystal structure of the title compound has been investigated as part of a programme of studies of captodative substituent effects on the cyclopropane geometry (Tinant, Declercq & Van Meerssche, 1984; Tinant, Wu, Declercq, Van Meerssche, De Mesmaeker, Masamba, Merenyi & Viehe, 1984). It is a well established fact that the cyclopropane ring undergoes significant geometrical changes under the influence of neighbouring π centres. For electron-withdrawing substituents the distal ring bond is shortened and vicinal bonds are lengthened (Allen, 1980; Ramasubbu, Rajaram & Venkatesan, 1982). Data for electron-donor and mixed donor–acceptor substituents are more sparse but results for *gem*-halogeno substitution indicate distal-bond lengthening (Allen, 1980; Deakye, Allen & Craig, 1977).

Our objective is to analyse the effects of *gem*-donor–acceptor or captodative (*cd*) substitution ($c = \text{CN}, \text{COOCH}_3, \dots$; $d = \text{SR}, \text{OR}, \dots$) on the ring bond pattern of the cyclopropyl ring. In previous papers we have reported the crystal structures of *cis*- and *trans*-2-*tert*-butyl- (or 2-phenyl-)thio-1,2-dicyanocyclopropanes. Now we wish to examine the effects of a Cl atom combined with *cd* substituents.

Experimental. Crystals obtained by evaporation from ether–petroleum ether. D_m not measured. Parallelepiped crystal with dimensions 0.2 × 0.2 × 0.4 mm. Lattice parameters refined using 15 reflections in range $5 \leq 2\theta \leq 25^\circ$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. $1830 \pm hkl$ independent reflections with $\sin\theta/\lambda \leq 0.561$ Å⁻¹; $-10 \leq h \leq 10$, $0 \leq k \leq 24$, $0 \leq l \leq 6$; 1313 with $I \geq 2.5\sigma(I)$. Standard reflection (002) checked every 50 reflections: no significant deviation. No absorption correction. Structure solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Cyclopropyl H atoms from difference Fourier synthesis. Anisotropic least-squares refinement (*SHELX76*, Sheldrick, 1976) using *F*. Cyclopropyl H isotropic with common fixed temperature factor, $B = 3.95$ Å²; other H computed with C–H = 1.08 Å. $w = 1/(\sigma^2 + 0.00033F^2)$, $R = 0.044$, $R_w = 0.045$ for 1313 observed reflections, $S = 2.27$. Final max. Δ/σ 0.78. Max. and min. heights in final difference Fourier