

occurs through the H(31) and O(17) atoms. N(3)—H(31)···O(17<sup>i</sup>) and H(31)···O(17<sup>i</sup>) distances and N(3)—H(31)···O(17<sup>i</sup>) angle [symmetry element (i): 2-x, -y, 1-z for *E*- and -x, 1-y, 1-z for *Z*-isomer] are 2.85 (1), 2.01 (6) Å and 165 (6)° for the *E*-isomer and 2.81 (1), 1.92 (8) Å and 163 (8)° for the *Z*-isomer respectively.

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## Structure of 9-Nitro-7*H*-dibenzo[*a,k*]anthracen-7-one

BY SHOJI FUJISAWA, ISAO OONISHI AND JUNJI AOKI

*Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan*

AND YUJI OHASHI

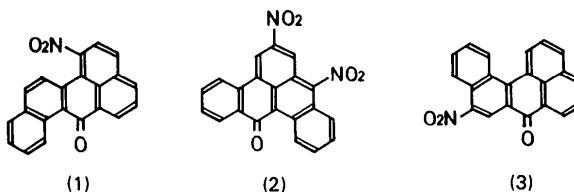
*Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka 2-1-1, Bunkyo-ku, Tokyo 112, Japan*

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**Abstract.** C<sub>21</sub>H<sub>11</sub>NO<sub>3</sub>, *M<sub>r</sub>* = 325.3, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 23.349 (9), *b* = 8.577 (4), *c* = 7.180 (3) Å, β = 97.62 (4)°, *V* = 1424.7 (10) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.49, *D<sub>x</sub>* = 1.517 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 0.109 mm<sup>-1</sup>, *F*(000) = 672, *T* = 298 K. Final *R* = 0.069 for 2226 independent reflections. The molecule is greatly distorted from a planar structure owing to the overcrowding of H atoms. The mean planes of the two naphthalene moieties make an angle of 24.95 (5)°. The NO<sub>2</sub> group rotates around the C—N bond from a coplanar conformation. The torsion angle O—N—C—C is 30.1 (3)°.

**Introduction.** Aromatic nitro compounds such as 1-nitro-7*H*-benzo[*h,i*]chrysen-7-one (1) (Fujisawa, Oonishi, Aoki & Ohashi, 1987) and 6,8-dinitro-13*H*-dibenz[*a,de*]anthracen-13-one (2) (Fujisawa, Oonishi, Aoki & Ohashi, 1986) have been extensively used as starting materials in the synthesis of polycyclic aromatic compounds. It is often difficult, however, to assign the positions of the nitro groups by chemical

procedures. The present study reports the structure of the title compound (3).



**Experimental.** Orange plate-like crystals from chlorobenzene solution; *D<sub>m</sub>* by flotation in ZnCl<sub>2</sub> solution; systematic absences: *h*0*l*, *h* = 2*n* + 1, 0*k*0, *k* = 2*n* + 1; crystal dimensions 0.45 × 0.45 × 0.20 mm; Rigaku AFC-6 diffractometer; graphite monochromator; cell parameters refined by least-squares method on the basis of 20 independent 2θ values, 20 < 2θ < 26°; intensity measurement performed up to 2θ = 50°; *h* -31 to 32, *k* 0 to 12 and *l* 0 to 10; ω-2θ scan, scan speed 2° min<sup>-1</sup> (2θ), scan width (1.2 + 0.35 tanθ)°; background 5 s

Table 1. Final atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters,  $B_{eq}(\text{\AA}^2) (\times 10)$ 

$$B_{eq} = \frac{4}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$$

	x	y	z	$B_{eq}$
C(1)	551 (1)	3571 (4)	3761 (4)	36 (1)
C(2)	1119 (1)	4096 (4)	4227 (4)	44 (1)
C(3)	1568 (1)	3159 (4)	3971 (4)	45 (1)
C(4)	1928 (1)	537 (4)	3239 (4)	46 (1)
C(5)	1831 (1)	-985 (4)	2860 (4)	46 (1)
C(6)	1267 (1)	-1562 (4)	2640 (4)	38 (1)
C(7)	218 (1)	-1211 (3)	2591 (4)	33 (1)
C(8)	-829 (1)	-685 (3)	2293 (4)	32 (1)
C(9)	-1285 (1)	286 (4)	2093 (4)	32 (1)
C(10)	-1231 (1)	1926 (3)	1878 (4)	32 (1)
C(11)	-658 (1)	2531 (3)	1994 (4)	30 (1)
C(12)	-169 (1)	1522 (3)	2524 (4)	28 (1)
C(13)	423 (1)	2097 (3)	3059 (4)	30 (1)
C(14)	895 (1)	1042 (3)	3013 (4)	30 (1)
C(15)	1473 (1)	1596 (4)	3383 (4)	37 (1)
C(16)	804 (1)	-575 (3)	2707 (4)	30 (1)
C(17)	-263 (1)	-78 (3)	2495 (4)	28 (1)
C(18)	-1701 (1)	2946 (4)	1354 (4)	42 (1)
C(19)	-1611 (1)	4450 (4)	870 (4)	47 (1)
C(20)	-1057 (2)	5014 (4)	832 (4)	43 (1)
C(21)	-591 (1)	4086 (4)	1400 (4)	37 (1)
N	-1855 (1)	-469 (3)	2000 (3)	42 (1)
O(1)	122 (1)	-2611 (2)	2532 (3)	48 (1)
O(2)	-1906 (1)	-1798 (3)	1382 (4)	61 (1)
O(3)	-2254 (1)	250 (3)	2559 (3)	58 (1)

$B_{ij}$ 's are defined by:  $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2klB_{23} + 2hlB_{13} + 2hkB_{12})]$ .

before and after each scan; three standard reflections monitored every 100 reflections, no significant variation in intensities; 4324 unique reflections measured, 2226 with  $|F_o| > 3\sigma(|F_o|)$  considered observed and used for structure determination; corrections for Lorentz and polarization, absorption ignored; direct methods (*MULTAN78*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and subsequent difference Fourier calculation; block-diagonal least squares (*HBL5*; Ohashi, 1975) with anisotropic thermal parameters for all non-H atoms; H atoms derived geometrically (C-H 1.08 Å) and refined;  $\sum w(|F_o| - |F_c|)^2$  minimized with  $w = [\sigma^2(F_o) + (0.03F)^2]^{-1}$ ; max. ( $\Delta/\sigma$ ) 0.25; final  $R = 0.069$ ;  $wR = 0.064$ ; the  $R$  value is rather high because of poor crystallinity;  $\Delta\rho$  excursions in final difference map  $0.3 e \text{\AA}^{-3}$ ; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); calculations carried out on HITAC M-280 computer at the Computer Center of the University of Tokyo.

**Discussion.** The final atomic parameters for non-H atoms are given in Table 1.\* A projection of the structure along the  $c$  axis is shown in Fig. 1. There are

\* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms and equations of mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43662 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

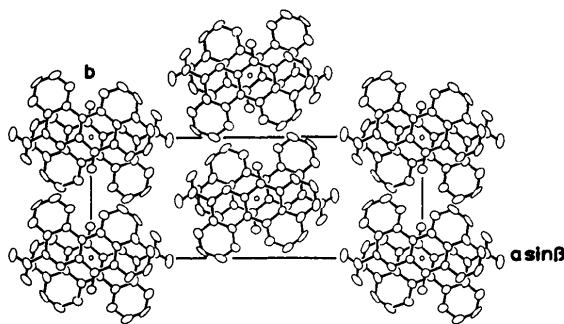
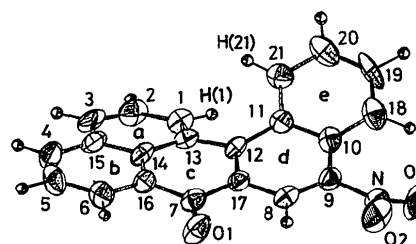
Fig. 1. A projection of the crystal structure along the  $c$  axis.

Fig. 2. Perspective drawing of the molecule and the numbering scheme.

Table 2. Bond lengths (Å) and angles ( $^\circ$ ) with their estimated standard deviations

C(1)–C(2)	1.397 (4)	C(10)–C(11)	1.428 (4)
C(1)–C(13)	1.379 (4)	C(10)–C(18)	1.414 (4)
C(2)–C(3)	1.353 (5)	C(11)–C(12)	1.442 (4)
C(3)–C(15)	1.414 (5)	C(11)–C(21)	1.415 (4)
C(4)–C(5)	1.347 (5)	C(12)–C(13)	1.470 (4)
C(4)–C(15)	1.411 (5)	C(12)–C(17)	1.389 (4)
C(5)–C(6)	1.396 (5)	C(13)–C(14)	1.429 (4)
C(6)–C(16)	1.378 (4)	C(14)–C(15)	1.421 (4)
C(7)–C(16)	1.465 (4)	C(14)–C(16)	1.415 (4)
C(7)–C(17)	1.480 (4)	C(18)–C(19)	1.359 (5)
C(7)–O(1)	1.222 (4)	C(19)–C(20)	1.383 (5)
C(8)–C(9)	1.345 (4)	C(20)–C(21)	1.367 (5)
C(8)–C(17)	1.408 (4)	N–O(2)	1.223 (4)
C(9)–C(10)	1.422 (4)	N–O(3)	1.228 (4)
C(9)–N	1.472 (4)		
C(2)–C(1)–C(13)	122.4 (3)	C(1)–C(13)–C(12)	123.6 (3)
C(1)–C(2)–C(3)	120.2 (4)	C(1)–C(13)–C(14)	117.3 (3)
C(2)–C(3)–C(15)	120.6 (4)	C(12)–C(13)–C(14)	118.9 (3)
C(5)–C(4)–C(15)	122.1 (4)	C(13)–C(14)–C(15)	119.9 (3)
C(4)–C(5)–C(6)	119.7 (4)	C(13)–C(14)–C(16)	121.6 (3)
C(5)–C(6)–C(16)	120.7 (3)	C(15)–C(14)–C(16)	118.4 (3)
C(16)–C(7)–C(17)	117.1 (3)	C(3)–C(15)–C(14)	122.8 (4)
C(16)–C(7)–O(1)	122.2 (3)	C(3)–C(15)–C(16)	118.7 (3)
C(17)–C(7)–O(1)	120.7 (3)	C(4)–C(15)–C(14)	118.4 (3)
C(9)–C(8)–C(17)	120.1 (3)	C(6)–C(16)–C(7)	120.0 (3)
C(8)–C(9)–C(10)	122.9 (3)	C(6)–C(16)–C(14)	120.4 (3)
C(8)–C(9)–N	115.5 (3)	C(7)–C(16)–C(14)	119.5 (3)
C(10)–C(9)–N	121.5 (3)	C(7)–C(17)–C(8)	117.2 (3)
C(9)–C(10)–C(11)	116.7 (3)	C(7)–C(17)–C(12)	122.0 (3)
C(9)–C(10)–C(18)	124.3 (3)	C(8)–C(17)–C(12)	120.7 (3)
C(11)–C(10)–C(18)	118.6 (3)	C(10)–C(18)–C(19)	120.9 (3)
C(10)–C(11)–C(12)	120.0 (3)	C(18)–C(19)–C(20)	120.9 (4)
C(10)–C(11)–C(21)	117.7 (3)	C(19)–C(20)–C(21)	120.0 (4)
C(12)–C(11)–C(21)	122.0 (3)	C(11)–C(21)–C(20)	121.5 (3)
C(11)–C(12)–C(13)	123.5 (3)	C(9)–N–O(2)	118.1 (3)
C(11)–C(12)–C(17)	118.1 (3)	C(9)–N–O(3)	118.9 (3)
C(13)–C(12)–C(17)	118.4 (3)	O(2)–N–O(3)	123.0 (3)

no unusually short contacts between the molecules. A perspective drawing of the molecule with the numbering scheme is shown in Fig. 2. Bond distances and angles are listed in Table 2. The NO<sub>2</sub> group is attached to the C(9) atom. The molecules are greatly distorted from a planar conformation because of the steric repulsion between H(C1)···H(C21), which is known as a 1,7 interaction, as in the structure of the parent 7H-dibenzo[*a,k*]anthracen-7-one (10,11-BzBT). The mean planes of the two naphthalene moieties [(*a,b*) and (*d,e*) rings in Fig. 2] make an angle of 24.95 (5)°. The repulsion is released mainly by the enlargement of the C(1)–C(13)–C(12), C(11)–C(12)–C(13) and C(12)–C(11)–C(21) angles and the distortion from a planar conformation. We have defined the degree of distortion as the twisting angle around the line C(11)···C(13). The torsion angle C(1)–C(13)···C(11)–C(21) is 36.7 (3)°, which is larger than that in 10,11-BzBT [33.4 (6)°] (Fujisawa, Oonishi, Aoki, Ohashi &

Sasada, 1985). The NO<sub>2</sub> group rotates around the C(9)–N bond from the coplanar conformation. The torsion angle O(2)–N–C(9)–C(8) is 30.1 (3)°.

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### Structure of 4-(4-Methoxyphenyl)thiosemicarbazide

BY D. CHATTOPADHYAY, T. BANERJEE AND S. K. MAJUMDAR

*Crystallography and Molecular Biology Division, Saha Institute of Nuclear Physics, Sector I, Block 'AF', Bidhannagar, Calcutta-700 064, India*

S. GHOSH

*Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta-700 032, India*

AND R. KURODA\*

*CRC Biomolecular Structure Unit, The Institute of Cancer Research, Sutton, Surrey SM2 5PX, England*

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**Abstract.** C<sub>8</sub>H<sub>11</sub>N<sub>3</sub>OS, *M<sub>r</sub>* = 197.26, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 13.105 (1), *b* = 5.759 (1), *c* = 13.056 (1) Å, β = 99.71 (2)°, *V* = 971.4 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.389, *D<sub>x</sub>* = 1.349 g cm<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 26.354 cm<sup>-1</sup>, *F*(000) = 416, *T* = 298 K, final *R* = 0.067 for 1499 observed reflections. There is significant electron localization at the hydrazinic end of the thiosemicarbazide side chain. This is due to the presence of the electron-releasing methoxy group in the phenyl ring *para* to the thiosemicarbazide chain and as a result the antibacterial activity of the compound increases.

**Introduction.** Thiosemicarbazides and thiosemicarbazones exhibit a variety of metal-chelating

capacities (Domiano, Gasparri, Nardelli & Sgarabotto, 1969; Nandi, Chaudhuri, Mazumdar & Ghosh, 1984*a,b*). The antibacterial, antiviral and anticancer activities possessed by substituted thiosemicarbazides and thiosemicarbazones have generated rapidly growing interest in the chemical, biochemical and structural aspects of these compounds (Johnson, Joyner & Perry, 1952; French & Blanz, 1966; Agrawal, Booth & Sartorelli, 1968; Agrawal, Cushley, McMurray & Sartorelli, 1970; Williams, 1972; Agrawal, Booth & Sartorelli, 1973; Kuroda, Neidle & Wilman, 1984). It has been suggested that the biological activities of these groups of N,S donor ligands originate from their metal-chelating and reductive capacities (Kirschner, Wei, Francis & Bergman, 1966; Palenik, Rendle & Carter, 1974). Comparative studies of the antibacterial activity of 4-phenylthiosemicarbazide and some of its ring-substituted derivatives revealed that the activity of the *para* methoxy and the *para* chloro derivatives

\* Present address: Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komba, Meguro, Tokyo 153, Japan.