

|        |              |            |            |           |
|--------|--------------|------------|------------|-----------|
| C(134) | -0.0634 (9)  | 0.8022 (5) | 0.5439 (5) | 0.074 (3) |
| C(135) | 0.0145 (8)   | 0.7398 (6) | 0.5456 (5) | 0.074 (3) |
| C(136) | 0.0349 (7)   | 0.6901 (5) | 0.4891 (4) | 0.063 (2) |
| C(137) | -0.0838 (10) | 0.8562 (6) | 0.6083 (5) | 0.113 (3) |
| C(211) | -0.1263 (7)  | 0.3104 (4) | 0.2639 (5) | 0.056 (2) |
| C(212) | -0.1896 (8)  | 0.3160 (5) | 0.2023 (5) | 0.070 (3) |
| C(213) | -0.3025 (9)  | 0.3500 (5) | 0.2049 (6) | 0.089 (3) |
| C(214) | -0.3506 (8)  | 0.3775 (6) | 0.2655 (8) | 0.102 (3) |
| C(215) | -0.2858 (8)  | 0.3711 (6) | 0.3259 (6) | 0.085 (3) |
| C(216) | -0.1740 (8)  | 0.3412 (5) | 0.3265 (5) | 0.077 (3) |
| C(217) | -0.4745 (8)  | 0.4119 (6) | 0.2696 (7) | 0.134 (3) |
| C(221) | 0.1780 (7)   | 0.2280 (5) | 0.2894 (4) | 0.050 (2) |
| C(222) | 0.2835 (8)   | 0.2577 (5) | 0.2748 (5) | 0.078 (3) |
| C(223) | 0.3786 (9)   | 0.2084 (7) | 0.2617 (6) | 0.104 (3) |
| C(224) | 0.3634 (10)  | 0.1275 (6) | 0.2625 (5) | 0.098 (3) |
| C(225) | 0.2557 (10)  | 0.0938 (6) | 0.2767 (5) | 0.085 (3) |
| C(226) | 0.1612 (8)   | 0.1446 (5) | 0.2899 (4) | 0.064 (3) |
| C(231) | 0.1728 (7)   | 0.3477 (5) | 0.3996 (4) | 0.054 (2) |
| C(232) | 0.2435 (7)   | 0.4135 (5) | 0.4022 (5) | 0.066 (2) |
| C(233) | 0.3323 (7)   | 0.4210 (5) | 0.4517 (5) | 0.071 (3) |
| C(234) | 0.3532 (8)   | 0.3632 (6) | 0.5016 (5) | 0.077 (3) |
| C(235) | 0.2814 (10)  | 0.2976 (6) | 0.4994 (5) | 0.103 (3) |
| C(236) | 0.1934 (9)   | 0.2896 (5) | 0.4504 (5) | 0.093 (3) |
| C(237) | 0.4487 (8)   | 0.3721 (6) | 0.5569 (5) | 0.105 (3) |

Table 2. Selected geometric parameters (Å, °)

|                     |            |                     |            |
|---------------------|------------|---------------------|------------|
| N(11)—C(12)         | 1.359 (11) | N(11)—C(111)        | 1.424 (11) |
| N(13)—C(12)         | 1.299 (12) | N(13)—C(131)        | 1.409 (11) |
| N(21)—C(22)         | 1.376 (10) | N(21)—C(211)        | 1.400 (10) |
| N(23)—C(22)         | 1.263 (10) | N(23)—C(231)        | 1.391 (10) |
| C(12)—C(121)        | 1.503 (12) | C(22)—C(221)        | 1.481 (11) |
| C(12)—N(11)—C(111)  | 128.4 (7)  | C(12)—N(13)—C(131)  | 116.5 (7)  |
| C(22)—N(21)—C(211)  | 128.6 (7)  | C(22)—N(23)—C(231)  | 120.1 (7)  |
| N(11)—C(12)—N(13)   | 120.9 (7)  | N(11)—C(12)—C(121)  | 112.7 (8)  |
| N(13)—C(12)—C(121)  | 126.2 (8)  | N(21)—C(22)—N(23)   | 120.7 (7)  |
| N(21)—C(22)—C(221)  | 113.0 (6)  | N(23)—C(22)—C(221)  | 126.2 (7)  |
| N(11)—C(111)—C(112) | 125.2 (7)  | N(11)—C(111)—C(116) | 114.9 (7)  |

The crystal was mounted in a Lindemann tube. The scan speed was 5–29° min<sup>-1</sup> in  $\omega$ , depending upon the intensity of a 2 s prescan; backgrounds were measured at each end of the scan for  $\frac{1}{4}$  of the scan time. Reflections were processed using profile analysis. The structure was solved by direct methods using *SHELXTL-Plus* (Sheldrick, 1986). Anisotropic temperature factors were used for all non-H atoms. H atoms were given fixed isotropic temperature factors,  $U = 0.08 \text{ \AA}^2$ . Those defined by the molecular geometry were inserted at calculated positions and not refined; Me groups were treated as rigid CH<sub>3</sub> units. The absolute structure was not determined. Computation was performed with *SHELXTL-Plus* on a DEC MicroVAX II.

We thank the SERC for grants in support of this work and the Associated Octel Co. Ltd for technical assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71593 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1054]

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## 2'-Bromo-4-[N-(2-cyanoethyl)-N-(2-phenylethyl)amino]-4'-nitroazobenzene

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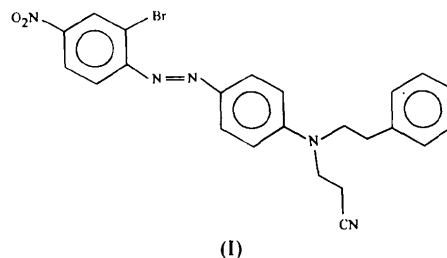
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## Abstract

The structure of the title compound 3-{{4-(2-bromo-4-nitrophenylazo)phenyl}(2-phenylethyl)amino}propanenitrile, C<sub>23</sub>H<sub>20</sub>BrN<sub>5</sub>O<sub>2</sub>, shows characteristic features of azobenzene derivatives. The rings in the azobenzene frame are twisted by 28.4 (4) and 9.9 (4)° in relation to the azo group plane. The larger twist is associated with the nitrobenzene ring and correlates with a longer N—C bond.

## Comment

Crystals of the title compound (I) were obtained from a toluene solution of commercially available material (Samaronscharlach RGSL FH-Hoechst, C.I. Disperse Red 183) by evaporation of the solvent.



The most interesting feature of the structure is the significant twist of one of the phenyl rings within the azobenzene frame. Only nine azobenzene structures among 21 entries found in the Cambridge Structural Database (1992) show significant conjugation of the whole azobenzene system, as evidenced by planarity and shortening of the two N—C bonds. In these structures, the values of both C—C—N—N torsion angles are below 8° and the average N—C bond length is 1.405 (8) Å. In eight other structures, the C—C—N—N torsion angles are greater (usually over 40°) and the average C—N bond length is 1.445 (5) Å (Table 2). There are also azobenzene derivatives with only one benzene ring coplanar with the azo system, similar to the title compound. The nitro group is twisted by 3.7 (2)° in relation to the

adjacent phenyl ring plane. Refinement of the cyanoethyl group at the isotropic stage gave an unreasonable C(24)—C(25) bond length of 1.41 (3) Å and valence angles of 99 (2)° at C(24) and 101 (2)° at C(25) due to considerable freedom of movement of the group in the crystal. The more 'normal' values were obtained after refinement with anisotropic displacement parameters. The phenylethyl group shows smaller mobility and 'better' geometry. The shortest intermolecular contact detected in the structure is 3.022 (1) Å for Br⋯H—C(5).

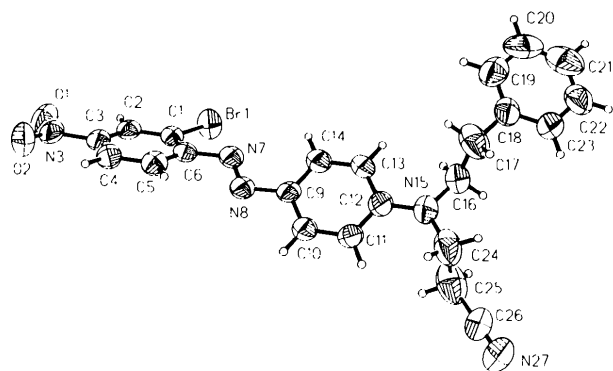


Fig. 1. A view of the title molecule. Anisotropic displacement ellipsoids are at the 50% probability level. H atoms are shown as spheres of arbitrary size.

## Experimental

### Crystal data

C<sub>23</sub>H<sub>20</sub>BrN<sub>5</sub>O<sub>2</sub>

*M<sub>r</sub>* = 478.4

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 18.938 (4) Å

*b* = 7.112 (1) Å

*c* = 16.205 (3) Å

β = 90.91 (3)°

*V* = 2182.3 (7) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.456 Mg m<sup>-3</sup>

Cu Kα radiation

λ = 1.5418 Å

Cell parameters from 25 reflections

θ = 25–35°

μ = 2.81 mm<sup>-1</sup>

*T* = 293 K

Plate

0.38 × 0.21 × 0.07 mm

Red

### Data collection

Kuma KM-4 diffractometer

ω/2θ scans

Absorption correction:

empirical (DIFABS;  
Walker & Stuart, 1983)

*T<sub>min</sub>* = 0.18, *T<sub>max</sub>* = 0.71

6175 measured reflections

3545 independent reflections

2526 observed reflections

[*F* > 6σ(*F*)]

*R<sub>int</sub>* = 0.040

θ<sub>max</sub> = 75°

*h* = -23 → 23

*k* = 0 → 8

*l* = 0 → 20

2 standard reflections  
monitored every 100  
reflections

### Refinement

Refinement on *F*

*R* = 0.063

Δρ<sub>max</sub> = 0.53 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.91 e Å<sup>-3</sup>

*wR* = 0.082

*S* = 1.50

2526 reflections

301 parameters

Only H-atom *U*'s refined

*w* = 1/[σ<sup>2</sup>(*F*) + 0.0008*F*<sup>2</sup>]

(Δ/σ)<sub>max</sub> = 0.012

Extinction correction:

Larson (1967)

Extinction coefficient:

0.0010 (4)

Atomic scattering factors

from SHELXTL/PC

(Sheldrick, 1990)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

|       | <i>x</i>   | <i>y</i>    | <i>z</i>   | <i>U<sub>eq</sub></i> |
|-------|------------|-------------|------------|-----------------------|
| Br(1) | 0.4311 (1) | 0.0930 (1)  | 0.6257 (1) | 0.079 (1)             |
| C(1)  | 0.4900 (3) | 0.3019 (8)  | 0.6135 (3) | 0.048 (2)             |
| O(1)  | 0.6590 (3) | 0.2739 (11) | 0.4597 (3) | 0.096 (2)             |
| O(2)  | 0.6903 (3) | 0.5570 (11) | 0.4918 (4) | 0.115 (3)             |
| C(2)  | 0.5476 (3) | 0.2859 (9)  | 0.5618 (4) | 0.055 (2)             |
| C(3)  | 0.5894 (3) | 0.4392 (10) | 0.5509 (4) | 0.059 (2)             |
| N(3)  | 0.6512 (3) | 0.4212 (12) | 0.4962 (4) | 0.077 (2)             |
| C(4)  | 0.5781 (3) | 0.6066 (11) | 0.5900 (4) | 0.064 (2)             |
| C(5)  | 0.5206 (3) | 0.6213 (9)  | 0.6417 (4) | 0.058 (2)             |
| C(6)  | 0.4778 (3) | 0.4686 (8)  | 0.6533 (3) | 0.050 (2)             |
| N(7)  | 0.4191 (3) | 0.4747 (7)  | 0.7087 (3) | 0.054 (2)             |
| N(8)  | 0.3929 (3) | 0.6369 (7)  | 0.7167 (3) | 0.054 (2)             |
| C(9)  | 0.3374 (3) | 0.6455 (8)  | 0.7733 (3) | 0.051 (2)             |
| C(10) | 0.3008 (3) | 0.8127 (10) | 0.7778 (4) | 0.062 (2)             |
| C(11) | 0.2457 (4) | 0.8343 (10) | 0.8317 (4) | 0.067 (2)             |
| C(12) | 0.2278 (4) | 0.6904 (10) | 0.8859 (4) | 0.065 (2)             |
| C(13) | 0.2659 (4) | 0.5225 (11) | 0.8812 (4) | 0.071 (3)             |
| C(14) | 0.3194 (4) | 0.5012 (10) | 0.8263 (4) | 0.067 (2)             |
| N(15) | 0.1736 (4) | 0.7088 (10) | 0.9399 (4) | 0.089 (3)             |
| C(16) | 0.1499 (4) | 0.5567 (12) | 0.9940 (5) | 0.084 (3)             |
| C(17) | 0.1865 (6) | 0.5560 (16) | 1.0769 (5) | 0.100 (4)             |
| C(18) | 0.1600 (4) | 0.4008 (12) | 1.1318 (4) | 0.070 (2)             |
| C(19) | 0.1978 (5) | 0.2382 (15) | 1.1440 (6) | 0.092 (4)             |
| C(20) | 0.1726 (7) | 0.0965 (16) | 1.1940 (7) | 0.110 (5)             |
| C(21) | 0.1085 (7) | 0.1170 (18) | 1.2303 (7) | 0.111 (5)             |
| C(22) | 0.0708 (5) | 0.2741 (18) | 1.2177 (5) | 0.102 (4)             |
| C(23) | 0.0948 (4) | 0.4127 (13) | 1.1680 (5) | 0.084 (3)             |
| C(24) | 0.1407 (5) | 0.9020 (17) | 0.9568 (5) | 0.103 (4)             |
| C(25) | 0.0825 (6) | 0.9024 (18) | 0.8997 (6) | 0.116 (5)             |
| C(26) | 0.0434 (6) | 1.0961 (18) | 0.9206 (7) | 0.130 (5)             |
| N(27) | 0.0120 (4) | 1.2230 (13) | 0.9315 (5) | 0.115 (4)             |

Table 2. Comparison of selected geometric parameters (Å, °) of the title compound and three other azobenzenes

|                         | (a)        | (b)       | (c)       | (d)       |
|-------------------------|------------|-----------|-----------|-----------|
| C(6)—N(7)               | 1.440 (8)  | 1.432 (3) | 1.403 (1) | 1.438 (7) |
| N(7)—N(8)               | 1.263 (7)  | 1.227 (3) | 1.274 (1) | 1.278 (7) |
| N(8)—C(9)               | 1.408 (8)  | 1.393 (3) | 1.393 (1) | 1.363 (7) |
| C(24)—C(25)             | 1.428 (13) |           |           |           |
| C(25)—C(26)             | 1.602 (17) |           |           |           |
| C(6)—N(7)—N(8)          | 113.5 (5)  |           |           |           |
| N(7)—N(8)—C(9)          | 113.9 (5)  |           |           |           |
| N(15)—C(24)—C(25)       | 101.4 (8)  |           |           |           |
| C(24)—C(25)—C(26)       | 102.7 (9)  |           |           |           |
| C(5)—C(6)—N(7)—N(8)     | 28.5 (8)   | -50.4 (5) | 38.4 (3)  | -91.4 (5) |
| C(6)—N(7)—N(8)—C(9)     | -177.5 (5) |           |           |           |
| N(7)—N(8)—C(9)—C(14)    | 10.2 (8)   | -2.9 (7)  | 6.8 (5)   | 1.0 (5)   |
| N(15)—C(24)—C(25)—C(26) | 175.8 (7)  |           |           |           |

Notes: (a) this study; (b) tri-*n*-butyl-6-(2-acetyl-amino-4-diethylamino-phenylazo)(3-bromo-5-methylphenyl)phosphonium bromide (Allen, Nowell, March & Taylor, 1984); (c) 3,5,8,16,19,22-hexaoxa-28-carboxy-29-hydroxy-12-(2,4-dinitrophenyldiazo)-*N*-tricyclo[23.3.1<sup>10,14</sup>]-nonacosane piperazine salt clathrate dichloromethane ethyl acetate solvate (Kaneda, Shizaki, Misumi, Kai, Hirao & Kasai, 1988); (d) 4-(2,6-dibromo-4-methylphenylazo)-3-hydroxy-*N,N*-diethylaniline (Connor, Kennedy, Dawes, Hursthouse & Walker, 1990).

High peaks on the  $\Delta F$  map were close to the Br atom. Calculations were carried out on a PS-2 computer using the *SHELXTL/PC* (Sheldrick, 1990) system. H atoms were allowed to ride at idealized distances from their associated C atoms.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71527 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1041]

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## Structure of Trijugin A

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## Abstract

In the title compound, methyl 11-acetoxy-10-(3-furyl)-12a-hydroxy-3,3,10a,12b-tetramethyl-13-methylene-4,8-dioxo-2,2a,3,4,5,5a,7,8,10,10a,11,12,-12a,12b-tetradecahydro-6a*H*-6a,12-methanofuro-[2,3,4-*fg*]pyrano[4,3-*b*][1]benzoxocine-2-carboxylate, C<sub>29</sub>H<sub>34</sub>O<sub>11</sub>, several C—C bonds and C—C—C angles

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‡ Contribution No. 826.

deviate by more than  $3\sigma$  from their expected values. The six-membered benzo and pyrano rings *A* and *D* are in distorted chair conformations. The five-membered furo and cyclopenta (formed by the methano bridge) rings *B* and *C* are in distorted half-chair conformations whereas the furyl ring *E* is planar within the  $5\sigma$  level. The title structure is stabilized by van der Waals forces.

## Comment

Trijugin A was isolated from the leaves of *H. trijuga* by Purushothaman, Mathuram, Sarada, Connolly & Rycroft (1987). This compound (**I**) represents a new skeletal type of tetranortriterpenoid which were found to be derivatives of methyl angolensate but with a novel carbon skeleton having a contracted ring *C*.

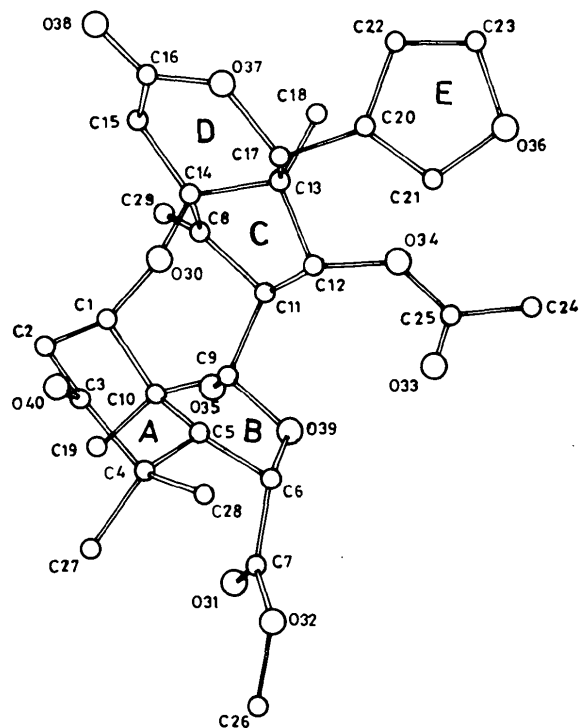
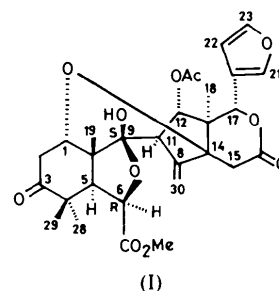


Fig. 1. View of the title molecule with the atom-numbering scheme.