

1.423 (3) Å] and invariably affects the bond angles: C(16)–C(8)–C(9), typically 121° in other MBA's, is reduced in 8-MBA to 118.9 (3)° and C(7)–C(16)–C(8) and C(8)–C(9)–C(10), typically 122.4 and 121.4°, are increased to 123.2 (3) and 122.5 (3)°, respectively. Although the *D* ring carries the substituent in 8-MBA, most of the deviations from the most reliable mean bond angles for type-I BA's (Briant *et al.*, 1985) are in or near ring *A*, namely enlargement by about 1° of angles C(2)–C(3)–C(4) and C(1)–C(13)–C(14), and reduction by about 1° of angles C(13)–C(1)–C(2), C(1)–C(2)–C(3), C(3)–C(4)–C(14), C(14)–C(5)–C(6), C(18)–C(13)–C(1), and C(10)–C(11)–C(17). <sup>1</sup>H NMR chemical shifts for 8-MBA in CS<sub>2</sub> solution are all within about 0.1 p.p.m. [or less for H(1–6) and H(12)] of the corresponding shifts in unsubstituted BA's (Jones & Mokoena, 1982; Evans, Fu & Cairns, 1981).

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## The Structure of a Tricyclic Peroxide\*

BY JOHN T. FOURKAS AND WILLIAM P. SCHAEFER

*Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, USA*

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**Abstract.** 10,11,14,15-Tetraoxa-1,8-diazatricyclo[6.4.4.0<sup>2,7</sup>]hexadeca-2(7),3,5-triene, BTDD, C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>, *M<sub>r</sub>* = 224.22, orthorhombic, *Pbca*, *a* = 7.635 (1), *b* = 11.041 (1), *c* = 24.249 (2) Å, *V* = 2044.1 (6) Å<sup>3</sup>, *Z* = 8, *D<sub>m</sub>* = 1.46 (3), *D<sub>x</sub>* = 1.46 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71073 Å, μ = 1.23 cm<sup>-1</sup>, *F*(000) = 944, *T* = 294 K, *R* = 0.0707 for 1785 reflections. The bridgehead N atoms adopt a nearly planar configuration [0.16 (1) and 0.10 (1) Å out of the planes of the C atoms to which they are bonded]. N–C and peroxide bonds are slightly short [N–C(–O) average 1.430 (3), N–C(–C) average 1.424 (4), O–O average 1.465 (10) Å], as expected from similar compounds. The four O atoms are disordered.

**Introduction.** Schaefer, Fourkas & Tiemann (1985) reported that the bridgehead N atoms of HMTD, hexamethylene triperoxide diamine, N(CH<sub>2</sub>OOCH<sub>2</sub>)<sub>3</sub>N (3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4.4.4]tetradecane), are coplanar with the C atoms to which they are bonded. We have synthesized several similar compounds to study this unusual nitrogen geometry. BTDD (benzene tetramethylene diperoxide diamine) is one such compound.

**Experimental.** 45 g H<sub>2</sub>O<sub>2</sub> and 60 ml formaldehyde solution (37%) are mixed and cooled to 273 K; 1 g *o*-phenylenediamine added, stirred for one hour; crystals collected, washed with ethanol; recrystallization from pentyl acetate; elemental analysis satisfactory for N, C, H; irregular crystal 0.33 × 0.33 × 0.44 mm; *D<sub>m</sub>* by flotation; Nonius CAD-4 diffrac-

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tometer; orthorhombic; intensity measurements with graphite-monochromated Mo  $K\alpha$  radiation,  $\theta$ - $2\theta$  scans,  $2^\circ \text{ min}^{-1}$  in  $2\theta$ , backgrounds measured for each reflection at each end of scan, average background as function of  $2\theta$  calculated and used to correct measured scan counts; unit cell: 25 reflections,  $19 < 2\theta < 21^\circ$ , least-squares refinement; max.  $(\sin \theta/\lambda)$   $0.59 \text{ \AA}^{-1}$ ; 3950 reflections in  $\pm h, k, l$  octants ( $h$  -9 to 9,  $k$  0 to 13,  $l$  0 to 28),  $4 < 2\theta < 50^\circ$ ; systematic absences  $0kl$ ,  $k$  odd,  $h0l$ ,  $l$  odd,  $hk0$ ,  $h$  odd indicate  $Pbca$ ; 1785 unique reflections used in structure solution and refinement, no reflections deleted;  $S_{\text{int}} = 1.03$   $\{S_{\text{int}} = [\sum w(F_o^2 - \bar{F}^2)^2 / (n-1)]^{1/2}\}$ ; structure solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); three check reflections monitored every 10 000 s, linear decay of  $0.14\% \text{ h}^{-1}$  ( $7.29\%$  total) in  $F$  magnitudes; no absorption correction applied,  $\mu r_{\text{max}} = 0.039$ ; H atoms placed at calculated positions, not refined ( $0.95 \text{ \AA}$  bond length used); 143 parameters refined minimizing  $\sum w(F_o^2 - F_c^2)^2$  with programs of *CRYM* system (Duchamp, 1964); form factors from *International Tables for X-ray Crystallography* (1974);  $R = 0.0707$  for  $F_o > 0$ ,  $S = 2.97$  from final converged least-squares fit; individual reflections assigned a weight  $w$  based on counting statistics plus a factor  $(0.014I)^2$  to account for errors proportional to intensity ( $0.014$  chosen by considering duplicate measurements); weights of merged reflections obtained by standard propagation of error plus an additional term,  $(0.014\bar{I})^2$ , to account for instrumental and other errors;  $(\Delta/\sigma)_{\text{max}} 0.07$ ;  $(\Delta\rho)_{\text{max}} 0.38$ ,  $(\Delta\rho)_{\text{min}} -0.52 \text{ e \AA}^{-3}$ ; O(1) and O(2) disordered between two orientations with populations  $0.835$  (8) and  $1 - 0.835$ ; O(3) and O(4) similarly disordered with populations  $0.588$  (7) and  $1 - 0.588$ ; this leads to a high  $R$  value; atomic coordinates given in Table 1,\* atom numbering shown in Fig. 1, selected bond distances and angles in Table 2; drawing made using *ORTEP* (Johnson, 1965).

**Discussion.** Despite the disorder in this molecule, we find the expected bond distances and angles. The weighted average of the O—O distances is  $1.464$  (10)  $\text{\AA}$ , close to the  $1.456$  (8)  $\text{\AA}$  observed in HMTD (Schaefer, Fourkas & Tiemann, 1985), and only slightly shorter than the  $1.47 \text{ \AA}$  in  $\text{H}_2\text{O}_2$  (Giguere & Schomaker, 1943). The N—C(—O) distances average  $1.424$  (3)  $\text{\AA}$ , compared to  $1.421$  (8)  $\text{\AA}$  in HMTD.

The nitrogen atoms, which are coplanar with the C atoms to which they are bonded in HMTD, are nearly coplanar in BTDD; N(1) is only  $0.16$  (1)  $\text{\AA}$  from the C(1), C(7), C(8) plane and N(2) is only  $0.10$  (1)  $\text{\AA}$

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond lengths and angles not involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42989 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

from the C(2), C(9), C(10) plane. The bond angles at N involving the benzene C atoms are smaller than those involving the peroxide rings, implying that the near planarity about the nitrogen atoms is associated with the peroxide groups, as expected from HMTD.

Table 1. Atomic parameters ( $x, y, z \times 10^4$ ;  $U$  and  $U_{\text{eq}}$  in  $\text{\AA}^2 \times 10^4$ )

|       | $x$       | $y$       | $z$      | $U$ or $U_{\text{eq}}$ |
|-------|-----------|-----------|----------|------------------------|
| C(1)  | 7955 (3)  | 2485 (2)  | 6098 (1) | 386 (6)*               |
| C(2)  | 9150 (3)  | 1559 (2)  | 5986 (1) | 383 (6)*               |
| C(3)  | 8882 (4)  | 820 (3)   | 5537 (1) | 484 (7)*               |
| C(4)  | 7442 (5)  | 969 (3)   | 5201 (1) | 577 (8)*               |
| C(5)  | 6249 (4)  | 1866 (3)  | 5315 (1) | 583 (8)*               |
| C(6)  | 6502 (4)  | 2615 (3)  | 5761 (1) | 497 (7)*               |
| C(7)  | 7778 (4)  | 2868 (3)  | 7093 (1) | 572 (8)*               |
| C(8)  | 9415 (4)  | 4262 (3)  | 6494 (3) | 572 (8)*               |
| C(9)  | 10344 (4) | 624 (3)   | 6817 (1) | 520 (7)*               |
| C(10) | 12141 (4) | 2084 (3)  | 6287 (1) | 586 (9)*               |
| N(1)  | 8207 (3)  | 3286 (2)  | 6556 (9) | 426 (5)*               |
| N(2)  | 10614 (3) | 1358 (2)  | 6341 (9) | 424 (5)*               |
| O(1A) | 9053 (3)  | 2124 (3)  | 7363 (1) | 513 (10)               |
| O(1B) | 7944 (23) | 1494 (14) | 7174 (6) | 708 (62)               |
| O(2A) | 8824 (3)  | 894 (3)   | 7131 (1) | 499 (10)               |
| O(2B) | 9671 (24) | 1475 (15) | 7302 (6) | 712 (56)               |
| O(3A) | 11011 (5) | 4027 (3)  | 6210 (2) | 541 (15)               |
| O(3B) | 11229 (7) | 3852 (5)  | 6655 (3) | 583 (20)               |
| O(4A) | 12017 (5) | 3254 (4)  | 6586 (2) | 551 (14)               |
| O(4B) | 11905 (7) | 3305 (5)  | 6144 (2) | 597 (22)               |

$$* U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*) a_i \cdot a_j]. \sigma U_{\text{eq}} = (\frac{1}{3})^{1/2} < \sigma U_{ii} / U_{ii} > U_{\text{eq}}.$$

Table 2. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

|                |           |                 |            |
|----------------|-----------|-----------------|------------|
| N(1)—C(1)      | 1.433 (3) | N(2)—C(10)      | 1.421 (4)  |
| N(1)—C(7)      | 1.421 (4) | O(1A)—O(2A)     | 1.481 (4)  |
| N(1)—C(8)      | 1.427 (4) | O(1B)—O(2B)     | 1.355 (23) |
| N(2)—C(2)      | 1.427 (3) | O(3A)—O(4A)     | 1.466 (5)  |
| N(2)—C(9)      | 1.426 (3) | O(3B)—O(4B)     | 1.472 (8)  |
| C(1)—N(1)—C(7) | 118.6 (2) | C(2)—N(2)—C(9)  | 117.6 (2)  |
| C(1)—N(1)—C(8) | 118.2 (2) | C(2)—N(2)—C(10) | 120.0 (2)  |
| C(7)—N(1)—C(8) | 119.4 (2) | C(9)—N(2)—C(10) | 120.9 (2)  |

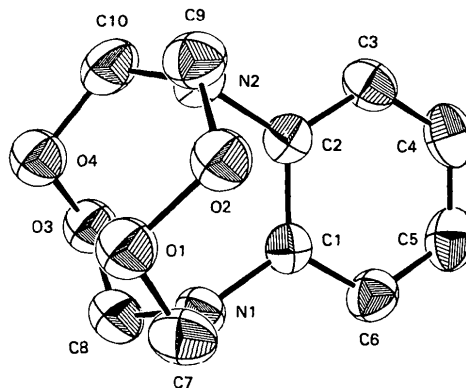


Fig. 1. Atom labelling for BTDD. The molecule shown has the larger population for the two peroxide bridges. Thermal ellipsoids are shown at the 50% probability level.

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## Benzoylimino-2 Triméthyl-1,4,6 Dihydro-1,2 Pyridine

PAR N. RODIER ET M.-P. GILLO

*Laboratoire de Chimie minérale, Faculté des Sciences pharmaceutiques et biologiques, rue J.-B. Clément, 92296 Châtenay-Malabry CEDEX, France*

ET S. PIESARD ET G. LE BAUT

*Laboratoire de Chimie thérapeutique, UFR de Pharmacie, 1 rue Gaston Veil, 44035 Nantes CEDEX, France*

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**Abstract.**  $C_{15}H_{16}N_2O$ ,  $M_r = 240.3$ , monoclinic,  $P2_1/c$ ,  $a = 7.301$  (3),  $b = 15.371$  (3),  $c = 11.347$  (5) Å,  $\beta = 95.90$  (4)°,  $V = 1267$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.260$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.075$  mm<sup>-1</sup>,  $F(000) = 512$ ,  $T = 294$  (1) K,  $R = 0.042$  for 1098 independent reflections. Interatomic distances and bond angles agree with previously published values. The molecule is almost planar. A delocalized orbital along the amide group is conjugated with the  $\pi$  electrons of the pyridinyl ring. The structure can be regarded as constituted by columns of molecules parallel with the  $a$  axis.

**Introduction.** A la suite d'une étude par les méthodes spectrographiques classiques (IR, RMN de <sup>1</sup>H et de <sup>13</sup>C, masse) (Bouhayat, 1981), le composé étudié ici a été considéré comme étant le *N*-méthyl *N*-(diméthyl-4,6 pyridinyl-2) benzamide. L'étude cristallographique a été entreprise dans le but de résoudre certaines difficultés d'interprétation des spectres de masse et de RMN du <sup>13</sup>C et de vérifier la structure moléculaire déjà admise. Elle a eu aussi pour objectif d'expliquer, à partir de la géométrie de la molécule, pourquoi ce composé présente une activité antiinflammatoire beaucoup plus modeste que le benzamide secondaire dont il est issu.

Le produit utilisé a été préparé par quaternisation, à 373 K, du *N*-(diméthyl-4,6 pyridinyl-2) benzamide en présence d'iodure de méthyle dans l'acétonitrile, suivie du passage à l'anhydro-base en milieu hydrogéné-

carbonate de sodium. Des cristaux ont été obtenus par évaporation lente d'une solution dans l'éthanol.

**Partie expérimentale.** Cristal prismatique: 0,26 × 0,26 × 0,32 mm. Dimensions de la maille déterminées sur monocristal avec 25 réflexions telles que  $5,29 \leq \theta \leq 12,17^\circ$ . Diffractomètre Enraf-Nonius CAD-4. Balayage  $\theta/2\theta$  d'amplitude  $s(^\circ) = 0,80 + 0,35 \text{tg}\theta$ .  $0,037 \leq (\sin \theta)/\lambda \leq 0,550$  Å<sup>-1</sup>,  $0 \leq h \leq 8$ ,  $0 \leq k \leq 16$ ,  $-12 \leq l \leq 12$ . Réflexions de contrôle: 040, 17 $\bar{3}$  et 200.  $\sigma(I)/I$  moyen (standards): 0,0023. 1750 réflexions indépendantes mesurées, 652 réflexions inobservées [ $I \leq 2\sigma(I)$ ]. Pas de correction d'absorption. Méthodes directes: programme *MULTAN11/82* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Atomes d'hydrogène: série de Fourier des ( $F_o - F_c$ ). Affinement basé sur les  $F$ . Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974). Paramètres affinés:  $x, y, z$  de tous les atomes et  $\beta_{ij}$  de C, N et O.  $wR = 0,047$ ,  $S = 1,56$ ,  $w = 1/\sigma^2(F)$ .  $(\Delta/\sigma)_{\max} = 0,33$ .  $|\Delta\rho|_{\max} = 0,23$  (3) e Å<sup>-3</sup>.  $g$  (extinction secondaire) =  $1,25 \times 10^{-6}$ . Programmes de calcul du système *SDP* (B. A. Frenz & Associates Inc., 1982). Dessin de la molécule: programme *ORTEP* (Johnson, 1965).

**Discussion.** Les coordonnées atomiques relatives sont rassemblées dans le Tableau 1, les principales distances