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The Structure of Hexamethylene Diperoxide Diamine

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Abstract. 3,4,8,9-Tetraoxa-1,6-diazabicyclo[4.4.2]do-decane(HMDD), $C_6H_{12}N_2O_4$, $M_r = 176.17$, monoclinic, $C2/c$, $a = 11.937(1)$, $b = 5.864(1)$, $c = 11.890(1)$ Å, $\beta = 110.00(1)^\circ$, $V = 782.1(3)$ Å³, $Z = 4$, $D_m = 1.44(2)$, $D_x = 1.50$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.35$ cm⁻¹, $F(000) = 376$, $T = 294$ K, $R = 0.0305$ for 681 independent reflections. The bridge-head N atoms adopt a nearly planar configuration [each is only 0.13(1) Å out of the plane of the C atoms to which it is bonded], as expected from similar compounds. N–C bonds to the peroxide bridges [average length 1.416(2) Å] are shorter than those to the all-carbon bridge [1.449(2) Å], again as expected from similar compounds.

Introduction. Schaefer, Fourkas & Tiemann (1985), Fourkas & Schaefer (1986), and Fourkas, Schaefer & Marsh (1987) have reported structures of three medium-ring bicyclic compounds with peroxide bridges: hexamethylene triperoxide diamine (HMTD, 3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4.4.4]tetradecane), benzene tetramethylene diperoxide diamine (BTDD, 10,11,14,15-tetraoxa-1,8-diazatricyclo[6.4.4.0^{2,7}]hexadeca-2(7),3,5-triene) and cyclohexane tetramethylene diperoxide diamine (CTDD, 10,11,14,15-tetraoxa-1,8-diazatricyclo[6.4.4.0^{2,7}]hexadecane), which have planar or nearly planar bridge-head N atoms. We have now synthesized an additional analogous compound, HMDD, in order to study further this unusual geometry.

Experimental. 45 g H₂O₂ (30% aqueous solution) and 60 ml formaldehyde solution (37%) were mixed and

cooled to 273 K; 2 ml ethylene diamine added, stirred for one hour; crystals collected, washed with ethanol; recrystallization from *n*-pentyl acetate; elemental analysis satisfactory for C, N, H; irregular crystal, 0.48 × 0.37 × 0.33 mm; D_m by flotation in an aqueous ZnBr₂ solution; Nonius CAD-4 diffractometer; monoclinic; intensity measurements with graphite-monochromated Mo $K\alpha$ radiation, θ - 2θ scans, 2° min⁻¹ in 2θ , backgrounds measured for each reflection at each end of scan, average background as a function of 2θ calculated and used to correct measured scan counts; unit cell: 25 reflections, $15 < 2\theta < 25^\circ$, least-squares refinement; max. $(\sin\theta)/\lambda$ 0.59 Å⁻¹; 2767 reflections collected over entire sphere with h –14 to 14, k –6 to 6, and l –14 to 14, $4 < 2\theta < 50^\circ$; three check reflections monitored every 10 000 s, intensities corrected for linear decay of 7.5% in F magnitudes; no absorption correction applied, $\mu r_{\text{max}} = 0.093$; individual reflections assigned a variance $1/w$ based on counting statistics plus a term $(0.014I)^2$ to account for errors proportional to intensity (0.014 chosen by considering duplicate measurements); systematic absences hkl , $h+k$ odd and $h0l$, l odd suggested $C2/c$; 681 independent forms used in structure solution and refinement, no reflections deleted; $S_{\text{int}} = 1.03$,

$$S_{\text{int}} = \left[\sum_{i=1}^N \left\{ \sum_{j=1}^M w_j (I_j - \bar{I})^2 / (M-1) \right\} / N \right]^{1/2},$$

where the outer sum is over the 681 independent forms and the inner sum is over all the equivalent reflections (usually 4) contributing to a form; variances of merged reflections obtained by standard propagation of error plus an additional term, $(0.014\bar{I})^2$, to account for other errors; structure solved with *MULTAN78* (Main, Hull,

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Lessinger, Germain, Declercq & Woolfson, 1978); 79 parameters refined minimizing $\sum w(F_o^2 - F_c^2)^2$ with programs of the *CRYM* system (Duchamp, 1964); form factors from *International Tables for X-ray Crystallography* (1974); $R = 0.0305$ for all $F_o^2 > 0$, $S = 3.79$ from final converged least-squares fit; $(\Delta/\sigma)_{\max} 0.06$; $\Delta\rho_{\max} 0.16$; $\Delta\rho_{\min} -0.19$ e \AA^{-3} ; atomic coordinates are given in Table 1, atom numbering is shown in Fig. 1, and selected bond distances and angles are given in Table 2; the drawing was made using *ORTEP* (Johnson, 1965).*

Discussion. The HMDD molecule is shown in Fig. 1. It lies on a twofold axis which passes through the dimethylene bridge C(1)–C(1').

This study provides the fourth example of the surprising phenomenon of a saturated compound with an approximately planar N atom. The common factor in all four of these compounds is the grouping N–CH₂–O–O–CH₂–N. The N atom in HMDD lies 0.127 (1) \AA from the plane of C(1), C(2) and C(3); similar out-of-plane distances are found for BTDD [0.102 (3) and 0.162 (2) \AA] and CTDD [0.135 (3) and 0.144 (3) \AA], whereas the nitrogen coordination is even more planar in HMTD [deviations of 0.008 (10) and 0.024 (10) \AA], in which all three bridges contain a peroxide group. It now seems clear that the peroxide groupings are primarily responsible for the near planarity of the N atoms; analogous compounds with all-C bridges show nearly normal tetrahedral N atoms (Alder, Orphen & Sessions, 1983).

Bond distances and angles in HMDD are given in Table 2. These values are considerably more precise than those found in the three other peroxo-bridged compounds. Two of these other compounds, BTDD and HMTD, suffered from disorder, and the third, CTDD, from crystal decay. Values in these other compounds generally agree with those in Table 2 within their e.s.d.'s. The most striking difference between the bond lengths in Table 2 and the average values found in a series of normal organic peroxides (Groth, 1967, 1969, 1975) is that at 1.415 (1) \AA the N–C bond adjacent to the peroxide group [N(1)–C(2)] is about 0.05 \AA shorter than a 'normal' bond of about 1.47 \AA ; the N(1)–C(1) bond adjacent to the methylene C atom shows a much smaller shortening. A possible explanation of the planar bonding about the N atom in valence-bond terms is that the non-bonding electrons on the N atoms have been partially hybridized into bonding sp^2 orbitals, with most of the additional bonding density appearing in the N–C(O) bond. The C

atom might then donate its excess electron density to the adjacent O atom, leading to partial 'non-bonding' character in the C–O bonds and to partial double-bond character in the O–O bonds. The O–O bonds are, indeed, marginally shorter than those in normal peroxides (1.465 vs 1.479 \AA), but there appears to be little lengthening of the C–O bond (1.437 vs 1.432 \AA). A more sophisticated study of the details of the electron distribution is still needed.

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

	x	y	z	U_{eq} or U
C(1)	9341 (1)	5503 (2)	2468 (1)	327 (3)*
C(2)	9253 (1)	2522 (2)	3885 (1)	323 (2)*
C(3)	8315 (1)	1851 (2)	1728 (1)	334 (3)*
N(1)	8866 (1)	3345 (2)	2695 (1)	275 (2)*
O(1)	9482 (1)	2326 (1)	546 (1)	355 (2)*
O(2)	9071 (1)	624 (1)	1219 (1)	364 (2)*
H(1)	11138 (13)	6028 (22)	3298 (14)	318 (27)
H(2)	10772 (12)	6636 (23)	1940 (12)	311 (27)
H(3)	11108 (12)	1065 (22)	1096 (12)	296 (26)
H(4)	10947 (12)	3569 (22)	585 (12)	316 (28)
H(5)	7745 (13)	2729 (24)	1069 (12)	278 (25)
H(6)	7928 (11)	605 (22)	2002 (10)	255 (25)

$$*U_{eq} = \frac{1}{3} \sum_i \sum_j |U_{ij}(a_i^* a_j^*) a_i \cdot a_j|. \sigma U_{eq} = (\frac{1}{6})^{1/2} < \sigma U_{ii}/U_{ii} > U_{eq}.$$

Table 2. Bond distances (\AA) and angles ($^\circ$)

C(1)–N(1)	1.449 (2)	C(3)–N(1)	1.417 (2)
C(1)–C(1)*	1.550 (2)	C(3)–O(2)	1.440 (1)
C(2)–N(1)	1.415 (1)	O(1)–O(2)	1.465 (1)
C(2)–O(1)	1.433 (1)		
O(1)–C(2)–N(1)	115.5 (1)	C(3)–N(1)–C(2)	120.2 (1)
N(1)–C(3)–O(2)	117.8 (1)	O(2)–O(1)–C(2)	107.0 (1)
C(2)–N(1)–C(1)	118.1 (1)	O(1)–O(2)–C(3)	105.3 (1)
C(3)–N(1)–C(1)	119.4 (1)	N(1)–C(1)–C(1)*	116.5 (1)
N(1)–C(1)–C(1)*–N(1)*	25.5 (1)	N(1)–C(3)–O(2)–O(1)	–58.1 (1)
N(1)–C(2)–O(1)–O(2)	–63.6 (1)	C(2)–O(1)–O(2)–C(3)	115.4 (1)

* These atoms are related by symmetry (a twofold axis).

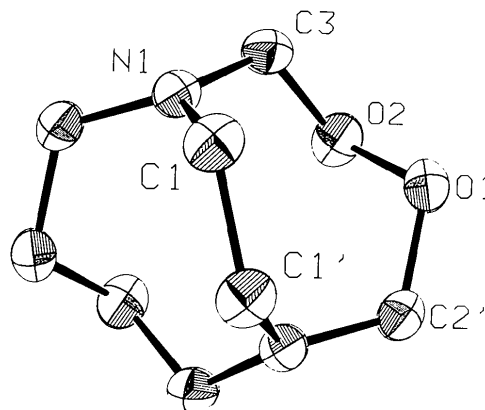


Fig. 1. Atom labelling for HMDD. Thermal ellipsoids are shown at the 70% probability level.

* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving hydrogen have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44139 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Crystal Studies of Heterocyclic Compounds Containing One Oxygen and Two Nitrogen Atoms. I. *N,N'*-Dibenzoylperhydro-1,4,5-oxadiazepine

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Abstract. C₁₈H₁₈N₂O₃, *M_r* = 310.4, monoclinic, *P*2₁, *a* = 13.000 (4), *b* = 6.271 (2), *c* = 10.240 (3) Å, β = 111.29 (2)°, *V* = 777.8 (6) Å³, *Z* = 2, *D_x* = 1.325 g cm⁻³, μ = 6.56 cm⁻¹. Diffractometer data collected at room temperature [λ(Cu Kα) = 1.54178 Å] consisted of 1651 independent reflections with *I* > 3σ(*I*). *F*(000) = 328; final *R* = 0.0435. The oxadiazepine ring is in the intermediate state between the chair and twist conformations. The benzoyl substituents are in equatorial configurations. There are no unusual bond lengths or angles.

Introduction. With the intention of searching for new substances with better therapeutic properties a series of new heterocyclic compounds containing five and more members and among them one O and two N atoms in the ring were obtained. The investigation of some of these compounds showed their neuroleptic and antiparasitic activity (Glinka, Kamińska, Kotelko & Szadowska, 1977; Glinka, Kotelko, Mikołajewska & Mikiciuk-

Olasik, 1979; Glinka, Grzywacz, Kotelko, Majchrzak, Malinowski, Mikołajewska, Mikiciuk-Olasik & Szkudlinski, 1980; Glinka, Szadowska & Pakulska, 1982). Some of the derivatives are under examination at the National Cancer Institute, Bethesda, Maryland, USA.

It is the aim of our X-ray structure investigation to find the three-dimensional structure of these compounds and to try to elucidate the structural dependence of their biological activity. The title compound has been investigated as the first of the series. It has been obtained by condensation of 2,2'-dichlorodiethyl ether with dibenzoylhydrazine. The formula was confirmed on the basis of IR, NMR and MS studies. The NMR spectrum of the compound seems to suggest that there are rotating conformers in solution.

Experimental. Colourless crystals grown from ethanol at room temperature, μ_r = 0.13; CAD-4 diffractometer, using θ–2θ scan technique; lattice parameters by least squares using 25 reflections with θ_{max} = 72.1°;