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150. Medium Ring Compounds. XXIX. Cyclooctane-1,5-dione-dioxime

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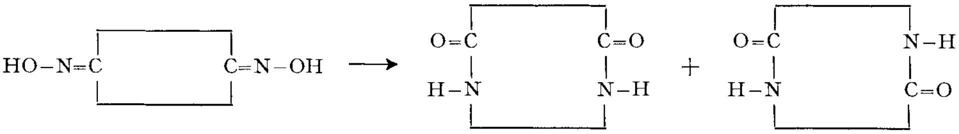
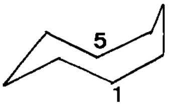
Summary. The crystal structure of the title compound (orthorhombic, $a = 26.724$, $b = 10.899$, $c = 9.483$ Å, space group $Pna2_1$, $Z = 12$) has been determined by X-ray analysis. The structural units consist of hydrogen-bonded trimers with approximate C_{3h} symmetry. The results are discussed in relation to the *Beckmann* rearrangement of the title compound, which yields exclusively the mirror-symmetric diamide.

The *Beckmann* or *Schmidt* rearrangements of symmetrical alicyclic diketoximes generally yield mixtures of the two possible isomeric cyclodiamides [1].



However, the eight-membered ring compound appears to be anomalous in this respect, for 1,5-cyclooctandione yields only the mirror-symmetric isomer, 1,5-diaza-6,10-cyclodecandione [2] [3]. No explanation for this has been proposed so far. *Glover et al.* only commented 'There may be a preference for the corresponding configuration of the dioxime, but models fail to show any' [3].

In this paper we describe the results of a crystal structure analysis of 1,5-cyclooctandione-dioxime. The structure has the unusual feature that the asymmetric unit of pattern consists of three independent molecules of dioxime (12 molecules in the unit cell). Our analysis shows that the three independent molecules all have virtually the same mirror-symmetric conformation **2**, which can be derived from the stable 'boat-chair' conformation of cyclooctane **1** [4] (which is also mirror-symmetric)



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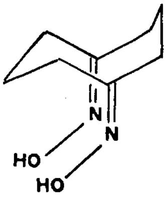

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by placing the substituents at the positions marked. Thus the mirror-symmetry of the stable conformation of cyclooctane seems to be preserved in the observed conformation of its 1,5-dione-dioxime, and hence it is not too surprising that it is also preserved in the rearrangement product.

The =N–OH substituents occur at the ring positions where transannular H ... H repulsion in cyclooctane is most severe. This energetically unfavourable interaction is erased when the two tetrahedral C-atoms are replaced by trigonal ring atoms, whereas it would be preserved if the trigonal atoms were introduced at other positions in the ring. The observed conformation **2** should thus be particularly favourable as far as ring-strain is concerned. The observed oxime configuration is also more favourable than the reversed one, which would lead to unduly short contacts between the O-atoms and the pseudo-axial H-atoms on the same side of the ring.

In the crystals, three molecules of dioxime are linked by a system of O–H ... N hydrogen bonds into distinct trimeric units. These trimers have approximate $C_{3h}(S_6)$ symmetry, the horizontal mirror plane corresponding to the approximate mirror plane of the individual molecules, which are then related to one another by the approximate threefold rotation axis.

Crystal data. – Cyclooctane-1,5-dione-dioxime, $C_8H_{14}N_2O_2$, Mol.-Wt. = 170.21, orthorhombic, $a = 26.724$, $b = 10.899$, $c = 9.483$ Å, space group $Pna2_1$ (C^9_{2v}), $Z = 12$, $D_x = 1.228$, $D_m = 1.23$.

Experimental. – Intensity data were collected out to $\theta = 25°$ with a *Hilger-Watts* Y290 diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) monochromatized by reflection from graphite. The crystal dimensions were 0.20×0.27×0.35 mm. Backgrounds were not measured individually but were interpolated from a curve of measured background versus θ. Out of 2585 independent reflexions measured, 2377 gave counts significantly above estimated background. The remaining 208 reflections were regarded as unobserved but were included in the refinement cycles if $|F_c| > |F_o|$.

Structure analysis and refinement. – The systematic absences [$(h0l)$ when l odd, $(0kl)$ when $k+l$ odd] are compatible with two possible space groups, $Pna2_1$ and *Pnam*; however, the statistical distribution of $|E|$-values clearly indicated a non-centrosymmetric structure so the latter possibility could be ruled out.

The structure was solved with the help of the automatic multisolution method MULTAN [5] and refined by full-matrix least-squares analysis. During the penultimate refinement cycles, hydrogen atoms were included in the model structure with isotropic temperature factors and refined, leading to a mean C–H distance of 1.02 Å (characteristically too short) and mean H–C–H angle of 106.8°, with several large individual discrepancies from these values. For the final cycles, the methylene H-atoms were included at calculated positions (based on assumed C_{2v} local symmetry of all CH_2 groups with the above mean C–H distance and H–C–H angle) and held constant; the oxime H-atoms were included at positions derived from an (F_o-F_c)-Fourier synthesis and allowed to vary, along with the 36 heavy atoms, which were given anisotropic temperature factors. A modified weighting system [6] with $r = 7$ Å^2 was used. The final R factor was 0.061 for the 2429 reflections included in the refinement. Form factors were taken from International Tables [7]. A list of observed $|F|$-values is available on request. Final positional and vibrational coordinates are given in Tables 1 and 2 (atomic numbering as in Fig. 1 for molecules A, B, C). Standard deviations in atomic positions, estimated by inversion of the least-squares normal equations are about 0.005 Å for N and O, and about 0.007 Å for C-atoms.

Table 1. *Atomic coordinates* (x 10^4) *and vibrational tensor components* (x 10^4) *for non-hydrogen atoms.* The U_{ij} values (in Å^2) correspond to the temperature factor expression $T = \exp\,[-2\pi^2\text{-}(U_{11}h^2a^{*2}+\ldots\,2U_{12}hka^*b^*\ldots)]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1A)	7662	1774	5250	495	357	392	29	2	4
O(1A)	7629	3014	4780	598	323	666	20	-109	-76
C(1A)	7387	1080	4435	431	377	327	-21	49	-13
C(2A)	7391	-279	4816	679	387	642	-107	-94	145
C(3A)	7482	-1102	3564	545	312	677	-78	-148	70
C(4A)	7995	-940	2872	538	350	564	45	-134	-19
C(5A)	8080	331	2272	422	373	312	10	-31	-78
C(6A)	7699	883	1273	497	441	399	-35	-73	-3
C(7A)	7378	1898	1968	513	369	497	21	-110	43
C(8A)	7071	1525	3238	428	400	653	20	-81	-10
N(2A)	8483	856	2649	420	444	441	-15	-14	-5
O(2A)	8541	2016	2001	558	559	721	-199	-103	161
N(1B)	8562	1740	7844	458	398	492	14	-6	-25
O(1B)	8154	958	7578	493	544	610	-45	-102	152
C(1B)	8890	1236	8624	509	444	295	72	34	11
C(2B)	9328	2019	9036	606	462	637	39	-149	-108
C(3B)	9841	1451	8709	507	469	570	-31	-108	-59
C(4B)	9943	1233	7172	493	535	714	-113	-41	31
C(5B)	9580	334	6477	402	446	390	61	-13	-24
C(6B)	9493	-877	7171	531	388	521	69	-10	-49
C(7B)	8980	-999	7872	567	362	652	-9	-10	22
C(8B)	8869	-83	9093	548	486	428	14	18	68
N(2B)	9388	679	5334	428	388	503	-5	-13	-66
O(2B)	9171	-213	4731	522	433	687	-32	-162	-35
N(1C)	8503	4285	5531	425	373	498	7	91	-4
O(1C)	8763	4081	6778	551	455	563	-56	-11	95
C(1C)	8646	5240	4865	430	382	566	37	108	-34
C(2C)	8368	5560	3535	463	509	654	36	0	70
C(3C)	8701	5944	2302	570	434	668	52	-68	82
C(4C)	9044	4918	1755	616	477	535	-19	34	-1
C(5C)	9388	4418	2846	404	411	560	-15	124	-7
C(6C)	9736	5267	3635	467	496	562	-110	49	54
C(7C)	9592	5508	5167	527	419	526	-141	-26	4
C(8C)	9062	6063	5392	607	377	479	-79	37	-84
N(2C)	9359	3264	3127	426	400	544	8	50	-39
O(2C)	9698	2880	4149	494	439	689	10	-50	66

Table 2. *Atomic coordinates* (x 10^4) *for hydrogen atoms*

	Molecule A			Molecule B			Molecule C		
	x	y	z	x	y	z	x	y	z
H(C2,1)	7658	– 435	5557	8 159	4823	3233	9 300	2841	8 527
H(C2,2)	7055	– 503	5262	8 125	6255	3746	9 307	2198	10 088
H(C3,1)	7445	–1992	3876	8 480	6240	1492	10 112	2012	9 101
H(C3,2)	7212	– 944	2827	8 916	6671	2601	9 871	637	9 231
H(C4,1)	8268	–1127	3593	8 830	4221	1367	9 932	2049	6 649
H(C4,2)	8033	–1572	2081	9 251	5244	932	10 300	905	7 063
H(C6,1)	7879	1237	416	10 087	4907	3607	9 534	–1556	6 437
H(C6,2)	7469	206	907	9 751	6086	3111	9 765	–1015	7 911
H(C7,1)	7611	2596	2258	9 614	4703	5709	8 712	– 891	7 113
H(C7,2)	7142	2244	1220	9 850	6086	5598	8 945	–1870	8 248
H(C8,1)	6862	2252	3561	9 012	6232	6439	8 524	– 264	9 502
H(C8,2)	6827	850	2948	9 043	6888	4887	9 121	– 219	9 888
H(O1)	7870	3380	5350	8 040	1300	6800	8 700	3250	7 250
H(O2)	8770	2300	2650	8 940	200	3850	9 600	2200	4 580

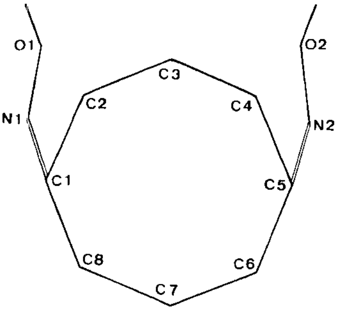

Fig. 1. *Atomic numbering*

Discussion. – The structural unit of the crystal consists of three approximately mirror-symmetric molecules linked by O–H ... N hydrogen bonds (mean length 2.78 Å) around an approximate threefold axis of symmetry. A stereoscopic view of the resulting trimeric unit is shown in Fig. 2. Such trimers also occur in crystalline acetoxime [8] where exact C_{3h} symmetry is imposed by the hexagonal space group ($P6_3/m$, $Z = 6$). In the present case, however, no crystallographic symmetry is imposed, and the C_{3h} symmetry is obeyed only in rough approximation.

Table 3 shows the atomic positions of the three molecules A, B, C in the asymmetric unit, each referred to a Cartesian coordinate system with origin at its molecular centre and with axes parallel to the geometric (mass unweighted) principal axes of the molecule. It is clear that the atomic coordinates of the three molecules, expressed in this way, are quite similar although by no means identical. The approximate mirror planes ($Y = 0$) pass through atoms C(3) and C(7).

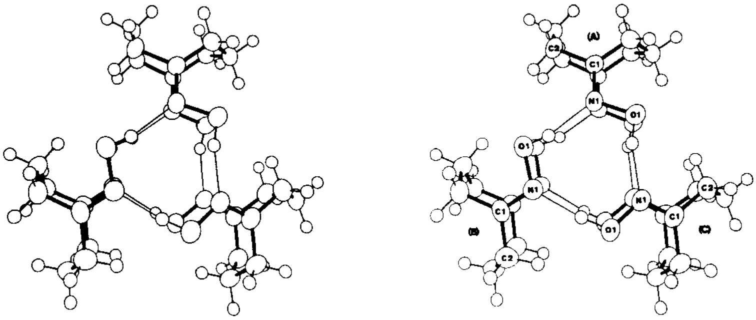

Fig. 2. *Stereoscopic view of the trimeric unit*

Table 3. *Coordinates of C, N, O atoms referred to principal axes* X, Y, Z *of the three individual molecules in the asymmetric unit.* The direction cosines of these axes with respect to the crystal axes are also listed

	Molecule A			Molecule B			Molecule C		
	X_A	Y_A	Z_A	X_B	Y_B	Z_B	X_C	Y_C	Z_C
N(1)	1.89	1.72	−0.12	1,87	1.68	−0.19	1.83	1.83	−0.18
N(2)	1.86	−1.73	−0.07	1.85	−1.76	−0.03	1.90	−1.58	−0.07
O(1)	2.26	1.83	−1.50	2.25	1.86	−1.53	2.18	2.04	−1.51
O(2)	2.28	−1.92	−1.41	2.28	−2.00	−1.35	2.35	−1.72	−1.38
C(1)	0.62	1.43	−0.03	0.62	1.46	−0.07	0.61	1.47	−0.03
C(5)	0.62	−1.45	0.00	0.63	−1.46	0.04	0.63	−1.43	0.03
C(2)	0.10	1.28	1.39	0.09	1.33	1.32	0.13	1.27	1.38
C(4)	0.07	−1.27	1.40	0.08	−1.23	1.45	0.05	−1.29	1.39
C(3)	−0.71	0.03	1.59	−0.71	0.05	1.59	−0.72	0.02	1.60
C(6)	−0.30	−1.31	−1.19	−0.30	−1.34	−1.12	−0.26	−1.31	−1.19
C(8)	−0.31	1.29	−1.19	−0.31	1.27	−1.24	−0.34	1.29	−1.19
C(7)	−0.09	0.01	−1.97	−0.09	−0.09	−1.97	−0.09	−0.02	−1.99
H(01)	3.18	1.91	−1.42	3.11	1.67	−1.45	3.18	2.18	−1.69
H(02)	3.17	−1.79	−1.23	3.26	−2.20	−1.25	3.20	−1.50	−1.47
Cell origin	−3.21	6.38	−0.29	−4.23	6.57	0.06	−4.26	5.78	−1.03
Direction cosines (x 10^4)									
a	7388	$\overline{6406}$	2092	$\overline{5407}$	$\overline{6120}$	5771	$\overline{1963}$	$\overline{6981}$	$\overline{6886}$
b	4739	2731	$\overline{8372}$	4482	3710	8133	$\overline{9520}$	3039	366
c	4792	7177	5053	7119	6984	747	2348	6484	$\overline{7242}$
Angles	$Y_AY_B = 5.9°$			$Y_BY_C = 6.9°$			$Y_CY_A = 5.4°$		
	$X_AX_B = 121.9°$			$X_BX_C = 119.2°$			$X_CX_A = 118.6°$		
	$Z_AZ_B = 121.5°$			$Z_BZ_C = 118.7°$			$Z_CZ_A = 118.6°$		

The deviations from exact C_{3h} symmetry of the trimeric unit are also evident from Table 4, where differences between 'symmetry equivalent' molecular parameters amount to about 0.04 Å for bond distances, 4.5° for bond angles and 10° for torsion angles. The mean dimensions of the oxime group agree quite well with those observed in other oximes [9].

The atoms C(1) and C(5), holding the oxime groups, appear to have the smallest vibrational amplitudes ($\langle U_{ii} \rangle = 0.042$ Å^2), closely followed by the N-atoms and

Table 4. *Bond distances* (in Å), *bond angles* (in deg.) *and torsion angles* (in deg.). Standard deviations in distances are about 0.007 Å where N or O atoms are involved, otherwise about 0.009 Å; in angles about 0.5° where N or O atoms are involved, otherwise about 0.7°. Values given are uncorrected for thermal motion effects

Distances (Å)	A	B	C	Mean	Range
O(1)–N(1)	1.426	1.407	1.390	1.406	0.036
O(2)–N(2)	1.414	1.411	1.391		
N(1)–C(1)	1.307	1.273	1.276	1.279	0.049
N(2)–C(5)	1.272	1.258	1.288		
C(1)–C(2)	1.524	1.498	1.504	1.509	0.040
C(5)–C(4)	1.514	1.528	1.488		
C(2)–C(3)	1.507	1.537	1.528	1.523	0.036
C(4)–C(3)	1.529	1.501	1.536		
C(1)–C(8)	1.495	1.505	1.515	1.505	0.022
C(5)–C(6)	1.514	1.493	1.510		
C(8)–C(7)	1.514	1.558	1.555	1.538	0.041
C(6)–C(7)	1.548	1.528	1.525		
O(1)–H	0.93	0.88	1.02		
N(1)A–O(1)B	2.72				
N(2)A–O(2)B	2.78				
N(1)B–O(1)C	2.80				
N(2)B–O(2)C	2.78			2.780	0.09
N(1)C–O(1)A	2.81				
N(2)C–O(2)A	2.79				
Angles (deg.)					
O(1)–N(1)–C(1)	109.3	112.1	113.7	112.2	4.4
O(2)–N(2)–C(5)	111.9	112.9	113.5		
N(1)–C(1)–C(2)	114.7	116.3	117.2	116.3	3.0
N(2)–C(5)–C(4)	115.6	116.1	117.7		
N(1)–C(1)–C(8)	125.3	123.9	122.7	124.0	3.2
N(2)–C(5)–C(6)	124.5	125.4	122.2		
C(8)–C(1)–C(2)	120.0	119.8	120.1	119.7	1.6
C(6)–C(5)–C(4)	119.9	118.5	120.0		
C(1)–C(2)–C(3)	113.1	114.5	114.7	113.9	1.6
C(5)–C(4)–C(3)	113.6	113.9	113.6		
C(2)–C(3)–C(4)	114.5	115.0	114.0	114.5	1.0
C(1)–C(8)–C(7)	112.6	112.6	113.2	113.4	2.4
C(5)–C(6)–C(7)	112.9	114.1	115.0		
C(6)–C(7)–C(8)	116.6	116.1	115.3	116.0	1.3
Torsion angles (deg.)					
O(1)–N(1)–C(1)–C(2)	–180.4	–176.8	–177.4	–178.3	3.0
O(2)–N(2)–C(5)–C(4)	177.8	178.0	179.3		
O(1)–N(1)–C(1)–C(8)	– 2.5	5.5	0.3	1.5	8.0
O(2)–N(2)–C(5)–C(6)	– 1.2	– 0.4	– 3.9		
C(1)–C(2)–C(3)–C(4)	63.7	62.8	65.1	62.3	6.5
C(5)–C(4)–C(3)–C(2)	– 62.1	– 61.7	– 58.6		
C(8)–C(1)–C(2)–C(3)	50.3	51.1	45.7	50.9	10.0
C(6)–C(5)–C(4)–C(3)	– 52.1	– 50.7	– 55.7		
C(7)–C(8)–C(1)–C(2)	–108.5	–105.8	–106.5	–106.9	2.8
C(7)–C(6)–C(5)–C(4)	105.7	107.5	107.2		
C(6)–C(7)–C(8)–C(1)	61.5	59.9	61.2	60.3	3.6
C(8)–C(7)–C(6)–C(5)	– 59.7	– 61.6	– 57.9		
C(1)–N(1)–O(1)–H	–172	–158	–170	–166	15
C(5)–N(2)–O(2)–H	160	179	157		

C(6), C(7), C(8) of the rings with $\langle U_{ii} \rangle = 0.044$–$0.046$ Å^2. The O-atoms and the carbon atoms C(2), C(3), C(4) show appreciably larger thermal motion (or disorder) with $\langle U_{ii} \rangle = 0.053$–$0.055$ Å^2.

Some aspects of the packing of the trimeric units are shown in the stereodiagram Fig. 3. The three molecules have quite different packing environments. Molecule A of the reference trimer sits above a hexagonal face of the trimer related by the *n/a* glide operation; the face built by the N(1) and O(1) atoms. Molecule B sits above the other hexagonal face (built by N(2) and O(2) atoms) of the trimer related by the screw axis. The C molecules merely help to fill up hydrocarbon layers at $y = 0$ and $y = 1/2$, each being in *van der Waals* contact with A, B and C molecules of other trimers. It is not so easy to see why trimers with C_{3h} symmetry should crystallize in a polar space group.

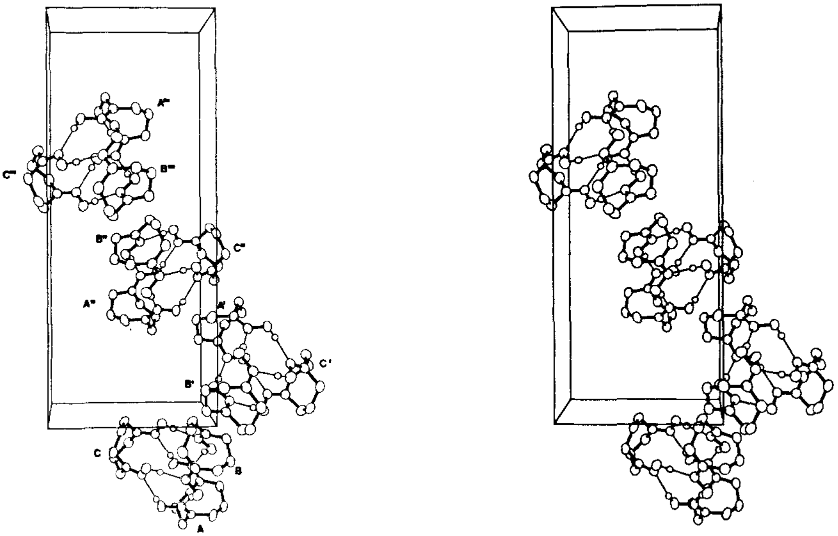

Fig. 3. *Stereoscopic view of the packing*; for clarity only four trimeric units are shown. The **a**-axis is vertical, the **b**-axis horizontal and the **c**-axis points upwards towards the viewer. The standard molecule (at *x, y, z*) is unprimed, those related by the 2_1, *a/b* and *n/a* operations being singly, doubly and triply primed respectively

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