Crystal and Molecular Structure of an Octamer of Acetonitrile Oxide

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Crystals of $(CH_3CNO)_8$ are monoclinic, space group $C2/c$, with $Z = 8$ in a unit cell of dimensions $a = 23.915(7)$, $b = 17.467(6)$, $c = 11.169(4)$ Å, $\beta = 100.71(6)$°. Diffractometer data yielded 2169 observed reflections. The structure was solved by direct methods and refined by a least-squares procedure to R 0.071. The molecule is a cyclic octamer of acetonitrile oxide with *anti*-CH_3 configuration at all double bonds.

FROM the reaction product obtained by trimethylamine-catalysed polymerization a hexamer, a heptamer, and an octamer of acetonitrile oxide, CH_3CNO, have been isolated.[1] These products appeared to be cyclic stereoregular polymers from spectroscopic evidence, since each exhibits only a singlet in its ^1H n.m.r. spectrum. From i.r., Raman, and u.v. spectra the octamer had to be formulated as 3,6,9,12,15,18,21,24-octamethyl-1,4,7,10,-13,16,19,22-octaoxa-2,5,8,11,14,17,20,23-octa-azacyclotetracosa-2,5,8,11,14,17,20,23-octaene, either *anti*-CH_3 (I) or *syn*-CH_3 (II) with respect to all the double bonds. Analogous molecular structures have been suggested for the hexamer and heptamer. Owing to the difficulty of otherwise establishing the correct geometrical conformation of these heteromacrocyclic compounds an X-ray analysis of at least one of them appeared to be worthwhile: the octamer (I) or (II) was chosen, because it gave suitable crystals (m.p. 171 °C, decomp.) on slow recrystallization from methanol.

EXPERIMENTAL

Crystals are transparent, mostly elongated in the c direction. X-Ray photographs showed a monoclinic symmetry; from systematic extinctions (hkl: $h + k = 2n$; $h0l$: $l = 2n$) the space group is $C2/c$ or Cc, the former being indicated from intensity statistics.[2]

Crystal Data.—$C_{16}H_{24}N_8O_8$, $M = 456.4$. Monoclinic, $a = 23.915(7)$, $b = 17.467(6)$, $c = 11.169(4)$ Å, $\beta = 100.71(6)$°, $U = 4\,584.4$ Å^3, $D_c = 1.323$ g cm^{-3}, $F(000) = 1\,920$. Space group $C2/c$ (C^6_{2h}, No. 15). Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 1.16 cm^{-1}.

Intensity Measurements.—Intensities were collected from a well-shaped crystal with a Philips PW 1100 four-circle computer-controlled diffractometer (Istituto di Mineralogia dell'Università di Perugia) by the ω—2θ scan technique. Of 7 182 reflections within the range $3° < \theta < 30°$ scanned, (scan speed 0.05° s^{-1}, scan range 1.2°, background measured on both sides of the peak), 2 880 intensities had $(I_{\rm peak} - 2\sqrt{I_{\rm peak}}) > I_{\rm back}$. A further selection was made on the basis of $\sigma(I)$, taking as observed only the 2 169 reflections with $I > 4\sigma(I)$. Intensities were corrected for Lorentz-polarization effects but not for absorption, which was negligible.

Structure Determination and Refinement.—The structure was solved with direct methods by use of the program MULTAN.[3] Since the complete set of intensities, up to sin θ (Mo-K_α) 0.50, was very numerous, an attempt was made taking into account reflections up to sin θ 0.37. Starting with E values of 300 reflections ($E > 1.58$) and accepting 2 000 phase relationships with the highest $E_hE_kE_{h-k}$ values in a fully automatic operation the program resulted in eight phase sets, the one with the highest ABSFOM (1.14) and lowest RESID (29.55) gave the correct signs. From the subsequent Fourier map all atoms except hydrogen were detected, R being 0.32. Scattering factor curves for carbon, nitrogen, and oxygen were taken from ref. 4 and for hydrogen from ref. 5. After two full-matrix least-squares cycles with isotropic temperature factors (R 0.138) anisotropic refinement was carried out in the block-diagonal approximation. After one cycle (R 0.119) a difference-Fourier synthesis gave indications of the positions of all 24 hydrogen atoms; two more cycles, varying positional and thermal parameters (isotropic for H), reduced R to 0.075.

Because of some inconsistencies in shifts, a mean thermal parameter B 7.45 Å^2 was imposed on H(1)—(3), H(6), H(23), H(24). A final cycle, all parameters being varied except for hydrogen atoms, led to R 0.071. A weight of $1/\sqrt{\sigma}$, with σ derived from counting statistics, was given to all observed reflections. About 20 reflections were judged to be affected by secondary extinction and were excluded from least-squares calculations. A final difference-Fourier synthesis showed no maxima attributable to other atoms, though some spurious positive and negative areas were still present.

Positional parameters are given in Table 1.

RESULTS AND DISCUSSION

The molecule is a cyclic octamer of acetonitrile oxide with *anti*-CH_3 configuration at all double bonds. A general view of the molecule showing the atom numbering, except for hydrogen atoms, is given in Figure 1. Bond lengths and angles (Tables 2 and 3) are in good agreement with accepted values. The C–H distances (not listed) range from 0.82 to 1.12 Å. The mean C–N (1.273, range 0.039 Å) and C–O distance (1.341, range 0.056 Å) are slightly shorter than corresponding values found for similar bonds.[6-8] Mean C–C and N–O distances are 1.506 (range 0.079) and 1.453 Å (range 0.061) respectively. The apparent shortening of the C–O bonds does not correspond to a lengthening of C–N distances or to coplanarity of the pertinent sp^2 system with the

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[1] A. Brandi, F. De Sarlo, and A. Guarna, *J.C.S. Perkin I*, 1976, 1827.

[2] I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Cryst.*, 1965, **19**, 713.

[3] Programs used: MULTAN, P. Main, M. M. Woolfson, and G. Germain, *Acta Cryst.*, 1971, **A27**, 368; ORFLS, W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, 1962, Oak Ridge National Laboratory, BONDLA (Bond distances and angles), ' X-Ray ' program system, ed. J. M. Stewart, University of Maryland Technical Report TR 192, version of June 1972; ORTEP, C. K. Johnson, Report ORNL 3794, 1965, Oak Ridge National Laboratory, Tennessee.

[4] ' International Tables for X-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

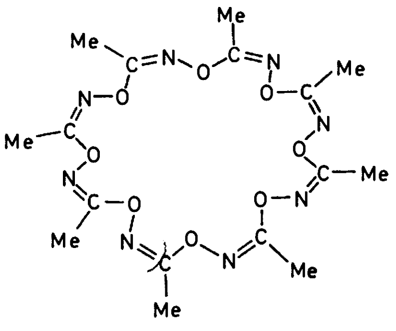
[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] G. Germain and D. Viterbo, *Cryst. Struct. Comm.*, 1972, **1**, 411.

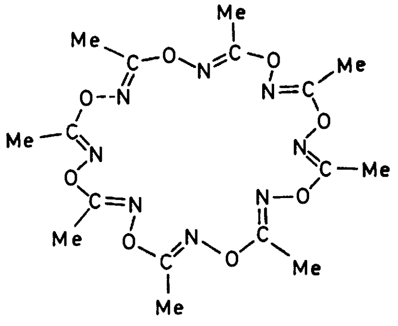
[7] A. F. Cameron and A. A. Freer, *Acta Cryst.*, 1974, **B30**, 354.

[8] M. Cannas and G. Marongiu, *Z. Krist.*, 1968, **127**, 388.

adjacent N atom, so that no important delocalization of the double bond seems to have occurred.



(I)



(II)

The pentatomic groups O(1)–N(1)–C(1)–C(9)–O(2), O(2)–N(2)–C(2)–C(10)–O(3), *etc.* (Table 4) are roughly planar with observed deviations from mean planes of <0.07 Å. The deviation of each N atom from the least-squares plane of the adjacent group ranges from 0.062 to 0.780 Å. Similarly, dihedral angles between these mean planes show a large scattering of values, ranging from 6.3 to 65.8°. Because of these variations, which do not seem to follow any rule, the molecule has an

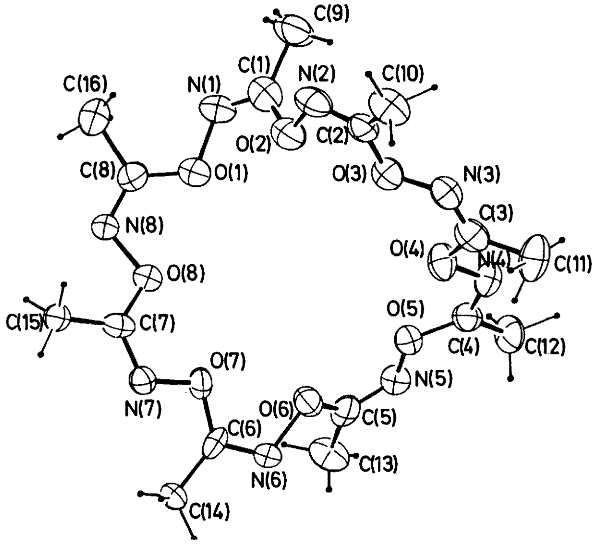


FIGURE 1 A perspective view of the molecule. Non-hydrogen atoms are shown as ellipsoids of 50% probability

TABLE 1

Fractional co-ordinates ($\times 10^4$, H $\times 10^3$), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
O(1)	899(2)	1 650(2)	1 289(4)
O(2)	1 826(2)	1 335(2)	660(4)
O(3)	2 794(2)	1 858(2)	875(4)
O(4)	3 225(2)	2 600(2)	2 751(4)
O(5)	2 813(2)	3 218(2)	4 450(4)
O(6)	1 929(2)	4 048(2)	4 141(4)
O(7)	1 025(2)	4 120(2)	2 563(4)
O(8)	529(2)	2 982(2)	1 439(4)
N(1)	1 061(2)	826(3)	1 330(5)
N(2)	2 128(2)	1 159(3)	−334(5)
N(3)	3 370(2)	2 123(3)	916(5)
N(4)	3 569(2)	2 566(3)	3 974(4)
N(5)	2 631(2)	3 483(3)	5 530(4)
N(6)	1 596(2)	4 753(3)	4 086(4)
N(7)	553(2)	4 286(3)	1 591(4)
N(8)	120(2)	2 413(3)	957(5)
C(1)	1 534(3)	753(4)	956(7)
C(2)	2 610(3)	1 486(3)	−175(6)
C(3)	3 557(3)	2 462(4)	1 900(6)
C(4)	3 325(2)	2 867(3)	4 797(6)
C(5)	2 194(2)	3 914(3)	5 309(6)
C(6)	1 155(2)	4 751(3)	3 246(5)
C(7)	324(2)	3 667(3)	1 098(5)
C(8)	343(3)	1 766(4)	950(6)
C(9)	1 761(3)	−66(4)	926(9)
C(10)	2 937(3)	1 456(4)	−1 178(6)
C(11)	4 176(3)	2 739(4)	2 095(6)
C(12)	3 624(3)	2 812(4)	6 071(6)
C(13)	1 977(3)	4 243(4)	6 363(6)
C(14)	812(2)	5 455(3)	3 123(6)
C(15)	−191(2)	3 769(3)	87(6)
C(16)	−41(3)	1 073(4)	488(8)
H(1) *	210	5	115
H(2)	165	−13	10
H(3)	145	−31	135
H(4)	332	114	−81
H(5)	277	118	−188
H(6)	302	200	−151
H(7)	436	238	270
H(8)	402	306	135
H(9)	400	325	225
H(10)	364	330	648
H(11)	407	258	612
H(12)	339	249	642
H(13)	201	471	632
H(14)	154	412	626
H(15)	217	410	709
H(16)	48	537	331
H(17)	77	568	229
H(18)	100	591	361
H(19)	−28	430	−16
H(20)	−8	351	−66
H(21)	−53	345	41
H(22)	4	090	130
H(23)	−31	141	7
H(24)	19	96	−25

* σ on H atom parameters 2, 3, and 5 on *x*, *y*, *z*.

TABLE 2

Intramolecular bond distances (Å)

C(1)–N(1)	1.283(10)	C(5)–N(5)	1.274(8)
C(1)–O(2)	1.311(9)	C(5)–O(6)	1.361(9)
C(1)–C(9)	1.531(10)	C(5)–C(13)	1.487(10)
N(2)–O(2)	1.466(9)	N(6)–O(6)	1.462(6)
C(2)–N(2)	1.270(8)	C(6)–N(6)	1.274(10)
C(2)–O(3)	1.341(8)	C(6)–O(7)	1.343(7)
C(2)–C(10)	1.481(12)	C(6)–C(14)	1.469(8)
N(3)–O(3)	1.444(6)	N(7)–O(7)	1.443(10)
C(3)–N(3)	1.256(9)	C(7)–N(7)	1.288(8)
C(3)–O(4)	1.367(10)	C(7)–O(8)	1.320(7)
C(3)–C(11)	1.536(9)	C(7)–C(15)	1.520(12)
N(4)–O(4)	1.459(10)	N(8)–O(8)	1.428(7)
C(4)–N(4)	1.290(9)	C(8)–N(8)	1.251(8)
C(4)–O(5)	1.361(7)	C(8)–O(1)	1.327(8)
C(4)–C(12)	1.472(11)	C(8)–C(16)	1.548(10)
N(5)–O(5)	1.433(7)	N(1)–O(1)	1.489(6)

TABLE 3

Intramolecular bond angles (°)

N(1)–C(1)–O(2)	123.3(6)	N(5)–C(5)–O(6)	120.4(6)
N(1)–C(1)–C(9)	115.9(6)	N(5)–C(5)–C(13)	118.0(5)
O(2)–C(1)–C(9)	120.8(6)	O(6)–C)(5)–C(13)	121.6(5)
C(1)–O(2)–N(2)	112.8(5)	C(5)–O(6)–N(6)	109.7(4)
O(2)–N(2)–C(2)	111.2(5)	O(6)–N(6)–C(6)	113.4(4)
N(2)–C(2)–O(3)	118.9(6)	N(6)–C(6)–O(7)	119.6(5)
N(2)–C(2)–C(10)	118.1(6)	N(6)–C(6)–C(14)	115.9(6)
O(3)–C(2)–C(10)	123.0(5)	O(7)–C(6)–C(14)	124.5(4)
C(2)–O(3)–N(3)	109.8(5)	C(6)–O(7)–N(7)	109.3(4)
O(3)–N(3)–C(3)	111.1(5)	O(7)–N(7)–C(7)	111.3(4)
N(3)–C(3)–O(4)	122.3(5)	N(7)–C(7)–O(8)	122.1(5)
N(3)–C(3)–C(11)	116.7(6)	N(7)–C(7)–C(15)	116.1(5)
O(4)–C(3)–C(11)	121.0(5)	O(8)–C(7)–C(15)	121.8(5)
C(3)–O(4)–N(4)	110.1(4)	C(7)–O(8)–N(8)	109.3(4)
O(4)–N(4)–C(4)	113.5(4)	O(8)–N(8)–C(8)	111.6(5)
N(4)–C(4)–O(5)	118.9(5)	N(8)–C(8)–O(1)	122.9(5)
N(4)–C(4)–C(12)	117.4(5)	N(8)–C(8)–C(16)	118.7(5)
O(5)–C(4)–C(12)	123.7(6)	O(1)–C(8)–C(16)	118.4(5)
C(4)–O(5)–N(5)	107.7(4)	C(8)–O(1)–N(1)	113.5(4)
O(5)–N(5)–C(5)	113.2(5)	O(1)–N(1)–C(1)	109.0(5)

TABLE 4

(*a*) Equations of least-squares planes in the form $PI + QJ + RK = S$, where I, J, K are co-ordinates in Å

Plane (1): $0.308I + 0.091J + 0.947K = 2.193$
Plane (2): $-0.333I + 0.850J - 0.407K = 0.218$
Plane (3): $-0.233I + 0.861J - 0.452K = 0.873$
Plane (4): $0.495I + 0.860J - 0.121K = 7.106$
Plane (5): $0.588I + 0.809J - 0.022K = 7.830$
Plane (6): $0.660I + 0.358J - 0.660K = 1.994$
Plane (7): $0.743I + 0.047J - 0.667K = -0.099$
Plane (8): $-0.315I - 0.180J + 0.932K = 0.215$

(*b*) Deviation (Å) of atoms from planes

Plane (1): O(1) −0.011, N(1) 0.018, C(1) −0.011, C(9) −0.004, O(2) 0.009, N(2) * −0.767

Plane (2): O(2) 0.060, N(2) −0.067, C(2) −0.025, C(10) 0.048, O(3) −0.016, N(3) * −0.097

Plane (3): O(3) −0.026, N(3) 0.033, C(3) −0.001, C(11) −0.017, O(4) 0.010, N(4) * −0.780

Plane (4): O(4) −0.031, N(4) 0.038, C(4) 0.006, C(12) −0.023, O(5) 0.010, N(5) * −0.062

Plane (5): O(5) 0.016, N(5) −0.023, C(5) 0.004, C(13) 0.010, O(6) −0.008, N(6) * 0.529

Plane (6): O(6) 0.016, N(6) −0.022, C(6) 0.005, C(14) 0.009, O(7) −0.007, N(7) * 0.188

Plane (7): O(7) −0.016, N(7) 0.020, C(7) 0.001, C(15) −0.011, O(8) 0.006, N(8) * −0.340

Plane (8): O(8) 0.016, N(8) −0.022, C(8) 0.004, C(16) 0.009, O(1) −0.008, N(1) * 0.174

(*c*) Dihedral angles (°) between planes

(1)–(2) 65.8, (2)–(3) 6.3, (3)–(4) 47.1, (4)–(5) 8.3, (5)–(6) 46.2, (6)–(7) 18.5, (7)–(8) 30.2

* Atom not included in definition of plane.

irregular shape, like a dried leaf; in edge-on view it appears twisted helically like a figure-of-eight (Figure 2). Table 5 lists torsion angles. All contact distances are within expected values, with the exception of some N ··· H and H ··· H contacts which are a little shorter than the sum of the corresponding van der Waals radii. This might be ascribed to uncertainty in hydrogen-atom locations. Shortest intermolecular interactions are presented in Table 6. A list of observed and calculated structure factors and thermal parameters is included in Supplementary Publication No. SUP 21871 (22 pp., 1 microfiche).*

In addition to some local programs, programs for the CII 10070 computer are listed in ref. 3.

TABLE 5

Torsion angles (°) *

O(1)–N(1)–C(1)–O(2)	3.5	O(5)–N(5)–C(5)–O(6)	3.6
N(1)–C(1)–O(2)–N(2)	−146.6	N(5)–C(5)–O(6)–N(6)	−158.6
O(2)–N(2)–C(2)–O(3)	6.8	O(6)–N(6)–C(6)–O(7)	3.4
N(2)–C(2)–O(3)–N(3)	174.4	N(6)–C(6)–O(7)–N(7)	−173.2
O(3)–N(3)–C(3)–O(4)	−4.7	O(7)–N(7)–C(7)–O(8)	−2.8
N(3)–C(3)–O(4)–N(4)	146.7	N(7)–C(7)–O(8)–N(8)	166.0
O(4)–N(4)–C(4)–O(5)	−4.5	O(8)–N(8)–C(8)–O(1)	−3.5
N(4)–C(4)–O(5)–N(5)	178.6	N(8)–C(8)–O(1)–N(1)	173.9

* The angles A–B–C–D are counted positive when, looking along the central B–C bond, the far bond is rotated clockwise with respect to the near bond.

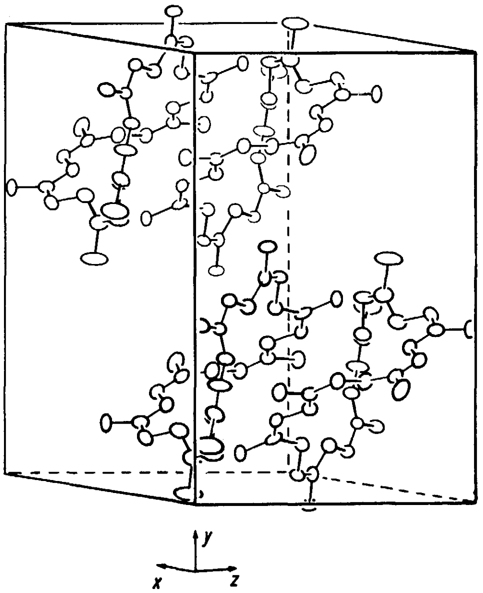


FIGURE 2 Molecular packing; for clarity, only four of the eight molecules in the unit cell are shown

TABLE 6

Selected intermolecular distances (Å)

O(1) ··· C(12$^{\text{II}}$)	3.103(13)	O(5) ··· N(5$^{\text{II}}$)	3.157(6)
O(2) ··· N(3$^{\text{III}}$)	3.204(7)	O(5) ··· C(9$^{\text{IV}}$)	3.219(9)
O(3) ··· O(3$^{\text{III}}$)	3.132(10)	N(2) ··· N(3$^{\text{III}}$)	3.250(8)
O(3) ··· C(2$^{\text{III}}$)	3.103(8)	N(2) ··· C(3$^{\text{III}}$)	3.237(11)
O(5) ··· O(5$^{\text{II}}$)	3.275(8)	N(5) ··· C(4$^{\text{II}}$)	3.256(8)
O(3) ··· H(15$^{\text{II}}$)	2.82(5)	O(8) ··· H(11$^{\text{II}}$)	2.89(5)
O(6) ··· H(12$^{\text{II}}$)	2.83(5)	N(1) ··· H(10$^{\text{II}}$)	2.87(5)
O(6) ··· H(5$^{\text{III}}$)	2.78(6)	N(3) ··· H(18)$^{\text{V}}$	2.59(5)
O(7) ··· H(4$^{\text{III}}$)	2.76(6)	N(8) ··· H(11$^{\text{VIII}}$)	2.56(5)
H(7) ··· H(20$^{\text{VII}}$)	2.57(6)	H(14) ··· H(17$^{\text{VI}}$)	2.37(7)
H(11) ··· H(21$^{\text{VII}}$)	2.25(7)	H(17) ··· H(19$^{\text{I}}$)	2.44(5)

Roman numeral superscripts define the following equivalent positions relative to the reference molecule at x, y, z:

I	$-x, 1 - y, -z$	V	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
II	$\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$	VI	$x, 1 - y, \frac{1}{2} + z$
III	$\frac{1}{2} - x, \frac{1}{2} - y, -z$	VII	$\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
IV	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	VIII	$-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$

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