

Acta Cryst. (1974). B30, 544

1,1,2-Trimorpholinoethene

By A. ALBINATI AND M. ZOCCHI

Istituto di Chimica Industriale del Politecnico, Sezione di Chimica Macromolecolare e Materiali, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

(Received 6 August 1973; accepted 20 September 1973)

Abstract. Monoclinic, $P2_1/c$, $a=10.717$ (2), $b=18.585$ (3), $c=8.673$ (2) Å, $\beta=115.87$ (7)°, formula unit $C_{14}H_{25}O_3N_3$, $Z=4$, $D_x=1.209$ g cm⁻³. The crystals were prepared by recrystallizing the product obtained by Ferruti, Segre & Feré [*J. Chem. Soc. (C)* (1968), pp. 2721–2725]. The morpholino groups, with chair conformation, are not equally bonded to ethene and there is evidence for electron delocalization on the N–C(ethene) bonds in the 1,1-substituents.

Introduction. The intensities of 2734 reflexions up to $2\theta=50^\circ$ (graphite-monochromated Mo $K\alpha$ radiation) were obtained from a crystal of 0.03 cm average linear dimension and of regular shape using a Philips four-circle automated diffractometer and the ω -scan technique (scan speed 1.8° min⁻¹), and by averaging two background counts (10 s each) for each reflexion. During data collection the intensities of three standard reflexions were measured every hour to monitor changes in the experimental conditions. No significant variation was detected. No absorption or extinction correction was found to be necessary.

1812 reflexions with integrated intensities greater than 2.5 $\sigma(I)$ were considered observed. The systematic absences were $h0l$ for l odd and $0k0$ for k odd.

The structure was solved by direct methods using the program *MULTAN* (Germain, Main & Woolfson,

1971) for choosing the starting set of signs and the program by Long (1965) for generating the list of the most probable sets of signs. All the non-hydrogen atoms in the structure appeared clearly in the E -map based on the set of signs with the highest figures of merit, and all the hydrogen atoms were located on a Fourier difference map after a preliminary refinement. Block-diagonal least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms (isotropic for the hydrogen atoms) and weights chosen after Cruickshank (1961) yielded final R values of 0.056 for the observed and 0.083 for both the observed and unobserved reflexions.

All the structure-factor, Fourier and least-squares computations were carried out with programs by Immirzi (1967, 1973).

The scattering factors of Hanson, Herman, Lea & Skillman (1964) for the non-hydrogen atoms and those of Stewart, Davidson & Simpson (1965) for hydrogen were used in the refinement. A final $F_o - F_c$ Fourier difference map showed no significant features.*

* A table of calculated and observed structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30231 (17 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final positional ($\times 10^4$) and thermal parameters

The anisotropic temperature factor is expressed as $T = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$. The e.s.d.'s are given in parentheses and refer to the last significant figures.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	9373 (2)	3889 (1)	1481 (3)	2.10 (10)	3.19 (10)	3.23 (11)	0.48 (15)	2.24 (16)	0.16 (17)
C(2)	10452 (3)	3957 (2)	3031 (4)	2.55 (10)	4.22 (13)	3.59 (12)	0.40 (18)	2.77 (18)	-0.73 (19)
C(3)	12185 (3)	3045 (2)	3957 (5)	3.15 (13)	4.47 (15)	7.79 (22)	0.88 (23)	2.82 (27)	0.23 (30)
C(4)	13644 (4)	2874 (2)	4192 (6)	3.66 (16)	6.33 (21)	9.47 (29)	3.22 (30)	2.39 (33)	-0.27 (40)
C(5)	14311 (3)	4068 (2)	4843 (5)	2.57 (12)	7.02 (21)	6.82 (21)	-0.46 (26)	2.56 (26)	-1.18 (34)
C(6)	12860 (3)	4263 (2)	4607 (5)	2.99 (12)	5.58 (17)	5.57 (17)	-0.82 (23)	2.46 (23)	-2.08 (28)
C(7)	7771 (3)	3824 (2)	2822 (4)	2.90 (11)	5.48 (15)	3.89 (13)	1.24 (21)	3.17 (20)	0.56 (23)
C(8)	6304 (3)	3543 (2)	2295 (5)	3.14 (13)	8.12 (23)	5.03 (16)	1.68 (28)	4.41 (24)	2.73 (31)
C(9)	5519 (3)	4069 (2)	-391 (5)	2.53 (12)	7.14 (20)	4.98 (16)	1.93 (24)	2.00 (22)	1.13 (29)
C(10)	6971 (3)	4352 (2)	20 (4)	2.39 (10)	5.05 (15)	4.10 (13)	0.85 (20)	1.97 (19)	1.66 (22)
C(11)	8841 (3)	1873 (2)	3995 (4)	4.20 (14)	4.18 (13)	3.90 (13)	1.30 (22)	3.96 (22)	0.99 (21)
C(12)	8563 (4)	1804 (2)	2146 (4)	5.74 (17)	4.85 (14)	4.02 (14)	2.26 (26)	4.77 (27)	1.60 (24)
C(13)	10308 (4)	942 (2)	2826 (4)	5.12 (16)	4.91 (16)	4.74 (15)	1.02 (26)	5.74 (26)	-0.09 (25)
C(14)	10665 (3)	993 (2)	4713 (4)	3.43 (12)	4.63 (14)	4.68 (14)	0.64 (21)	4.54 (23)	0.69 (23)
N(1)	11853 (2)	3785 (1)	3373 (3)	2.48 (9)	4.30 (11)	4.09 (11)	0.19 (16)	2.25 (16)	-0.48 (17)
N(2)	7996 (2)	3876 (1)	1302 (3)	2.43 (8)	4.11 (10)	3.08 (9)	0.83 (14)	2.27 (14)	0.29 (15)
N(3)	9417 (2)	1206 (1)	4906 (3)	3.10 (9)	3.63 (9)	3.23 (9)	0.80 (15)	3.13 (16)	0.72 (15)
O(1)	14637 (2)	3343 (2)	5376 (4)	2.79 (9)	8.41 (17)	7.01 (15)	1.82 (20)	1.21 (18)	0.24 (25)
O(2)	5295 (2)	4021 (2)	1105 (3)	3.11 (9)	8.32 (16)	5.56 (12)	2.26 (19)	3.95 (17)	1.74 (22)
O(3)	9786 (2)	1605 (1)	1974 (3)	5.73 (11)	5.18 (11)	3.96 (9)	-0.26 (18)	5.55 (17)	0.49 (16)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(C2)	1029 (3)	412 (2)	408 (4)	4.0 (7)
H(C3)	1210 (4)	298 (2)	518 (5)	6.3 (9)
H'(C3)	1158 (4)	272 (2)	321 (5)	7.6 (11)
H(C4)	1383 (5)	238 (3)	468 (6)	9.2 (13)
H'(C4)	1361 (5)	288 (3)	286 (6)	9.6 (13)
H(C5)	1502 (4)	439 (2)	579 (5)	7.0 (10)
H'(C5)	1437 (4)	413 (2)	366 (5)	6.7 (10)
H(C6)	1288 (4)	426 (2)	583 (5)	5.4 (8)
H'(C6)	1267 (4)	481 (2)	413 (5)	7.1 (10)
H(C7)	841 (4)	347 (2)	360 (4)	4.8 (8)
H'(C7)	787 (3)	430 (2)	333 (4)	4.1 (7)
H(C8)	614 (5)	297 (2)	180 (5)	7.7 (11)
H'(C8)	612 (4)	357 (2)	322 (5)	6.4 (10)
H(C9)	488 (3)	442 (2)	-123 (4)	4.6 (7)
H'(C9)	538 (4)	361 (2)	-104 (5)	5.5 (8)
H(C10)	711 (4)	486 (2)	52 (4)	5.2 (8)
H'(C10)	713 (3)	441 (2)	-107 (4)	4.5 (7)
H(C11)	799 (3)	197 (1)	409 (4)	3.2 (6)
H'(C11)	955 (4)	227 (2)	453 (4)	5.3 (8)
H(C12)	824 (4)	228 (2)	162 (5)	6.3 (9)
H'(C12)	786 (4)	139 (2)	161 (5)	6.3 (9)
H(C13)	962 (4)	53 (2)	232 (5)	6.0 (9)
H'(C13)	1115 (5)	81 (2)	261 (6)	8.1 (12)
H(C14)	1093 (3)	51 (2)	534 (4)	5.3 (8)
H'(C14)	1146 (4)	134 (2)	529 (4)	4.8 (7)

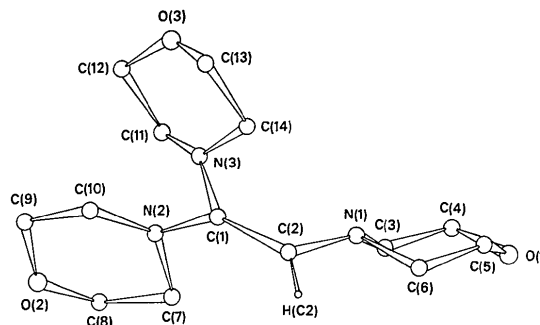


Fig. 1. Projection of the molecule on the plane defined by atoms N(1), N(2), N(3). The hydrogen atoms of the morpholino rings have been omitted for clarity.

given in Table 1; the bond distances and angles are presented in Tables 2 and 3; in Table 3 a selected list of internal rotation angles is also given in order to illustrate better some conformational details.

As shown in Fig. 1 and as it appears from the values listed in the Tables, the morpholino groups are in their chair conformation as expected (see *e.g.* Aroney, Chen, Le Fèvre & Saxby, 1964) and are not equally bonded to ethene. In fact for two of them (the 1,1 substituents) the N-C(ethene) distances are significantly shorter than the distance N(1)-C(2), the differences being equal to 4.5σ and 7.5σ respectively (σ is the standard deviation of the difference between distances). The molecular configuration helps to explain this result in terms of electron delocalization on the N(2)-C(1) and N(3)-C(1) bonds. In fact it is clear from Fig. 1 that the *p* orbitals of the electronic doublets on nitrogen atoms N(2) and N(3) are so directed that they must overlap to some extent the orbital of C(1) involved in the π bond in ethene. Obviously no possibility of overlap exists for the corresponding *p* orbitals of atoms N(1) and C(2). These electronic interactions, in their turn, help in explaining the geometrical differences among the three morpholino rings. In fact, while carbon atoms C(2), C(3), and C(6) are almost exactly at three vertices of a tetrahedron about nitrogen atom N(1) (the fourth vertex being presumably occupied by the electronic doublet), the geometrical arrangement about atoms N(2) and N(3) is far from tetrahedral, as shown by the values of the relevant C-N-C angles. These distortions propagate through the corresponding morpholino rings generating small but significant deformations even in the end parts of the rings about the oxygen atoms. On the other hand all the distances and angles in the ring unperturbed by these electronic interactions are equal, within two or three standard deviations, to already published values in comparable structures (see, *e.g.* Argay & Seres, 1973). We give evidence for the fact that at least in the crystal only two of the three morpholino groups are involved in the electronic interaction with the C=C π -orbital. Thus the n.m.r.

Table 2. Interatomic distances

C(1)—C(2)	1.347 (6) Å
C(3)—C(4)	1.520 (6)
C(5)—C(6)	1.520 (5)
C(7)—C(8)	1.525 (5)
C(9)—C(10)	1.530 (5)
C(11)—C(12)	1.503 (6)
C(13)—C(14)	1.513 (6)
N(1)—C(2)	1.442 (4)
N(1)—C(3)	1.456 (5)
N(1)—C(6)	1.446 (5)
N(2)—C(1)	1.415 (4)
N(2)—C(7)	1.443 (4)
N(2)—C(10)	1.470 (5)
N(3)—C(1)	1.398 (4)
N(3)—C(11)	1.456 (5)
N(3)—C(14)	1.472 (4)
O(1)—C(4)	1.412 (7)
O(1)—C(5)	1.418 (6)
O(2)—C(8)	1.432 (6)
O(2)—C(9)	1.421 (5)
O(3)—C(12)	1.431 (5)
O(3)—C(13)	1.420 (5)

Discussion. The n.m.r. study by Ferruti, Segre & Feré (1968) indicated that in 1,1,2-trimorpholinoethene the C=C bond is strongly perturbed by the electronic doublets of the nitrogen atoms and that the three morpholino groups are not all equivalent. We initiated the present analysis with the aim of finding evidence for this perturbation in the crystal, as a part of our structural studies of unsaturated hydrocarbons both in their free molecular state and in complexes with transition metals.

The atomic positional and thermal parameters are

Table 3. *Bond angles and internal rotation angles*

C(1)–C(2)–N(1)	122.69 (14)	C(10)–C(9)–O(2)	111.64 (15)
C(1)–C(2)–H(C2)	120.40 (212)	C(11)–N(3)–C(14)	110.96 (13)
C(1)–N(2)–C(7)	118.90 (13)	C(11)–C(12)–O(3)	111.64 (15)
C(1)–N(2)–C(10)	118.11 (15)	C(12)–C(11)–N(3)	110.25 (13)
C(1)–N(3)–C(11)	116.81 (12)	C(12)–O(3)–C(13)	109.92 (15)
C(1)–N(3)–C(14)	119.75 (13)	C(13)–C(14)–N(3)	109.04 (15)
C(2)–C(1)–N(2)	120.77 (13)	C(14)–C(13)–O(3)	111.40 (14)
C(2)–C(1)–N(3)	127.59 (14)	N(1)–C(2)–H(C2)	116.50 (152)
C(2)–N(1)–C(3)	112.08 (15)	N(2)–C(1)–N(3)	111.63 (11)
C(2)–N(1)–C(6)	112.12 (15)	C(4)–C(3)–N(1)–C(6)	58.14 (18)
C(3)–C(4)–O(1)	111.92 (16)	C(5)–C(6)–N(1)–C(3)	58.30 (19)
C(3)–N(1)–C(6)	109.42 (16)	C(9)–C(10)–N(2)–C(7)	56.72 (18)
C(4)–C(3)–N(1)	108.94 (14)	C(8)–C(7)–N(2)–C(10)	58.25 (20)
C(4)–O(1)–C(5)	110.47 (19)	C(12)–C(11)–N(3)–C(14)	55.17 (20)
C(5)–C(6)–N(1)	110.05 (13)	C(13)–C(14)–N(3)–C(11)	55.64 (22)
C(6)–C(5)–O(1)	111.24 (15)	C(3)–C(4)–O(1)–C(5)	57.60 (19)
C(7)–N(2)–C(10)	111.33 (14)	C(6)–C(5)–O(1)–C(4)	56.68 (20)
C(7)–C(8)–O(2)	111.05 (15)	C(7)–C(8)–O(2)–C(9)	61.12 (19)
C(8)–C(7)–N(2)	108.10 (14)	C(10)–C(9)–O(2)–C(8)	59.56 (21)
C(8)–O(2)–C(9)	108.84 (17)	C(11)–C(12)–O(3)–C(13)	58.55 (18)
C(9)–C(10)–N(2)	108.54 (13)	C(14)–C(13)–O(3)–C(12)	59.62 (20)

results have found here a clear structural interpretation with the implication that the molecular configuration in solution is essentially unchanged.

We thank Professor P. Ferruti and Dr A. Feré for having kindly prepared crystals suitable for X-ray analysis and Mr P. Zambelli for technical help. We also acknowledge financial support from the C.N.R., Rome, Italy.

References

- ARGAY, G. & SERES, J. (1973). *Acta Cryst.* B29, 1146–1149.
- ARONEY, M. J., CHEN, C. Y., LE FÈVRE, R. J. W. & SAXBY, J. D. (1964). *J. Chem. Soc.* pp. 4269–4274.
- CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Edited by PEPINSKY, R., ROBERTSON, J. M. & SPEAKMAN, J. C. Oxford: Pergamon.
- FERRUTI, P., SEGRE, A. & FERÉ, A. (1968). *J. Chem. Soc. (C)*, pp. 2721–2725.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* 17, 1040–1050.
- IMMIRZI, A. (1967). *Ric. Sci.* 37, 743–749.
- IMMIRZI, A. (1973). *J. Appl. Cryst.* 6, 246–249.
- LONG, R. (1965). Ph.D. Thesis, Univ. of California, Los Angeles.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.