1-(1-Morpholino-1-cyclohexen-6-ylideneammonio)-1-cyano-2-methoxy-2-oxoethanide. A stable azomethine ylide.

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Abstract

$C_{14}H_{19}N_3O_3$, orthorhombic, space group *Pbca*, $a = 23.37$ (3), $b = 9.25$ (2), $c = 13.77$ (1) Å, $Z = 8$. $D_c = 1.24$ Mg m^{-3}, μ(Mo $K\alpha$) = 0.095 mm^{-1}. The compound is a stable azomethine ylide. The structure was solved by direct methods and refined to $R = 0.084$ for 677 independent reflexions. This study has been carried out to confirm unambiguously the ylide structure of the compound.

Introduction

The isomerization of the azadiene (1), by refluxing in methanol, leads to the azomethine ylide (2). This compound is stable at room temperature and can be isolated in the crystalline form (Fleury, Schoeni & Clerin, 1975). Such behaviour is remarkable for a compound of this type

(1)   (2)
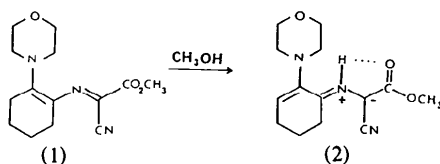
The study of the various spectroscopic data (IR, ^{1}H NMR and nuclear spin–spin coupling between ^{15}N and ^{13}C) (Clerin & Fleury, 1976) allows us to propose with substantial probability an azomethine ylide structure for compound (2). To our knowledge, a stable azomethine ylide with an N–H bond has not been described previously in the literature. Therefore it is interesting to verify such an unusual structure unambiguously, and to determine the geometry of the betainic part of the molecule.

Crystals were obtained by slow cooling of a hot saturated solution in methanol. The approximate dimensions of the sample used for the X-ray analysis are $0.4 \times 0.3 \times 0.25$ mm. Cell parameters were obtained from a least-squares refinement of the setting angles of 21 reflexions. Three-dimensional intensity data were collected on an Enraf–Nonius automatic three-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation and a $\theta/2\theta$ scan mode (scan range = $1.20°$). The crystal was a poor diffractor and only 677 reflexions had $I \geq 2\sigma(I)$; these were used in the structure determination.

The structure was solved from 123 reflexions with $E > 1.40$ using *MULTAN* (Germain, Main & Woolfson, 1971). The E map computed with the set of best consistency (COMBINED FOM = 2.2464) revealed the positions of 15 of the 20 heavy atoms. After a Fourier synthesis, the remaining heavy atoms were located.

Refinement of atomic positions and anisotropic temperature factors was carried out with the least-squares program

of Busing, Martin & Levy (1962). The following weighting scheme was introduced and used throughout refinement:

$$w^{-1} = \sigma^2(|F_o|) = \frac{1}{N}\frac{F_o^2}{4I^2}\left(CN + B + \frac{I^2}{400}\right),$$

where CN is the total number of counts collected during the scan, B is the total background counts, I is the net intensity and N the number of cycles of measurement for the reflexion. A difference Fourier synthesis revealed all the H atoms except those of the methyl group attached to the $C(10)$ atom. Because of the low number of reflexions, these H atoms were not refined, and were assigned mean isotropic temperature factors. Furthermore, because of the high thermal motion of the methyl group, the corresponding H atoms could not be located. The values of the final residuals $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = |\sum w||F_o| - |F_c||^2/\sum w|F_o|^2|^{1/2}$ are 0.084 and 0.076 respectively. The final atomic coordinates are given in Table 1 for the heavy atoms and in Table 2 for the H atoms. The bond distances and angles are shown in Fig. 1.*

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34386 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates with e.s.d.'s in parentheses*

	x	y	z
C(1)	0.8534 (4)	0.6595 (12)	0.8512 (8)
C(2)	0.8389 (5)	0.6975 (11)	0.9418 (9)
C(3)	0.7942 (6)	0.6207 (13)	0.9992 (7)
C(4)	0.7521 (5)	0.5391 (11)	0.9322 (8)
C(5)	0.7839 (4)	0.4422 (11)	0.8541 (7)
C(6)	0.8294 (4)	0.5302 (11)	0.8053 (6)
C(7)	0.8446 (4)	0.3714 (13)	0.6596 (8)
C(8)	0.8098 (5)	0.2497 (17)	0.6784 (8)
C(9)	0.8810 (5)	0.3816 (15)	0.5746 (10)
C(10)	0.9208 (5)	0.2644 (14)	0.4317 (8)
C(11)	0.9511 (4)	0.7679 (13)	0.8440 (7)
C(12)	0.9950 (5)	0.8145 (17)	0.7677 (10)
C(13)	0.9187 (5)	0.9091 (15)	0.6707 (9)
C(14)	0.8741 (5)	0.8601 (13)	0.7433 (9)
N(1)	0.8966 (3)	0.7290 (9)	0.7940 (6)
N(2)	0.8516 (3)	0.4930 (9)	0.7220 (5)
N(3)	0.7814 (4)	0.1468 (12)	0.6899 (7)
O(1)	0.8797 (3)	0.2611 (10)	0.5160 (5)
O(2)	0.9111 (3)	0.4898 (9)	0.5553 (5)
O(3)	0.9732 (4)	0.9448 (10)	0.7184 (7)

Table 2. *Atomic coordinates for hydrogen atoms*

	x	y	z
H(C2)	0·8566	0·7906	0·9752
H1(C3)	0·8112	0·5311	1·0403
H2(C3)	0·7723	0·6876	1·0504
H1(C4)	0·7206	0·4796	0·9705
H2(C4)	0·7324	0·6093	0·8839
H1(C5)	0·7563	0·4039	0·7976
H2(C5)	0·7964	0·3546	0·9002
H1(C11)	0·9703	0·6653	0·8713
H2(C11)	0·9437	0·8290	0·9085
H1(C12)	1·0347	0·8293	0·8019
H2(C12)	0·9994	0·7220	0·7197
H1(C13)	0·9274	0·8295	0·6147
H2(C13)	0·9056	1·0046	0·6322
H1(C14)	0·8337	0·8412	0·7065
H2(C14)	0·8653	0·9478	0·7931
H(N2)	0·8906	0·5312	0·7031

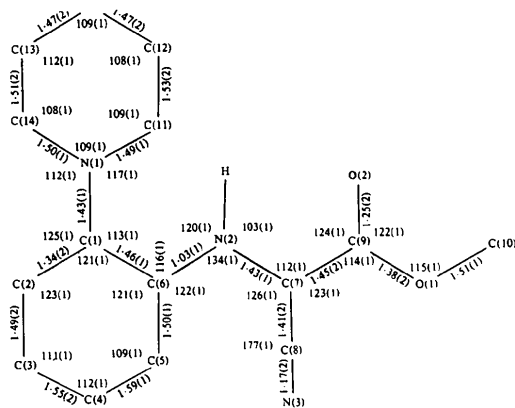Fig. 2. Perspective view of the molecule with thermal ellipsoids at 50% probability.

Fig. 1. The numbering system, bond lengths (Å) and valence angles (°) with standard deviations in parentheses.

Discussion

The X-ray analysis confirms unambiguously the structure deduced from the spectroscopic data. A drawing of the molecule made with *ORTEP* (Johnson, 1965) is shown in Fig. 2. The unexpected stability of this compound may be explained by the geometrical data. Although the hydrogen positions have not been refined, two intramolecular hydrogen bonds may be suggested for this compound, H(N2)···N(1) and H(N2)···O(2).
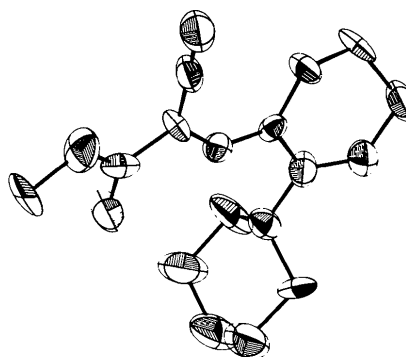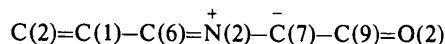
The conformation of the morpholino ring and the configuration of the N(1) atom are favourable to the formation of a hydrogen bond involving the lone pair: the distance between N(1) and O(2) is 3·98 Å. The hydrogen-bond system and the possible electronic delocalization on the

$$C(2)=C(1)-C(6)=\overset{+}{N}(2)-\overset{-}{C}(7)-C(9)=O(2)$$

chain may be sufficient to explain this stability.

The geometrical data also confirm the ylide character of the compound. Indeed the C(6)—N(2) bond (1·30 Å) is shorter than the N(2)—C(7) bond (1·43 Å) and these two bonds are of intermediate length between single and double bonds.

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