Preparation and X-Ray Structure Analysis of Methylenebis(3,3-diethylazetidine-2,4-dione)

George L. Buchanan and George A. Sim
Chemistry Department, University of Glasgow, Glasgow G12 8QQ

The compound obtained by condensing methylenediamine with diethylmalonyl dichloride has been shown by X-ray crystal-structure analysis to be methylenebis(3,3-diethylazetidine-2,4-dione). The four-membered ring is planar with C-N-C, N-C-C, and C-C-C angles of 94.4, 91.0, and 83.6°. Crystallographic data are a = 11.093(3), b = 7.239(2), c = 20.494(7) Å, β = 105.74(2)°, Z = 4, space group C2. X-Ray intensity measurements were made on a four-circle diffractometer and least-squares adjustment of the atomic parameters converged at R 0.040 for 1 540 reflections.

Recent investigations [1,2] of the synthesis and properties of the 1-azabicyclo[3.3.1]nonan-2-one system (1) have revealed that, unlike their all-carbon analogues,[3] these molecules prefer the boat-chair conformation and this result has been corroborated by X-ray crystallography.[4] Since the maintenance of approximate amide planarity appears to be the dominant factor in determining the conformation in (1), we were interested to discover whether a molecule, appropriately substituted with amide functionality in *both* rings, would be forced to adopt the novel boat-boat conformation.

Einhorn [5] has reported the synthesis of such a molecule (2) by condensing methylenediamine with diethylmalonyl dichloride, although no structural evidence was presented. We have been unable to repeat the synthesis under Einhorn's conditions which entailed generating methylenediamine by the action of base on the bisamide (3a). However, by following a more modern route [6] to the diamine, from the methylenebis-(formamide) (3b), we have isolated a neutral product having the same m.p. and the same elemental composition as Einhorn's. We now report that X-ray crystallography has shown that our product has the azetidinedione structure (4) and it seems probable that this also represents Einhorn's compound.

The X-ray intensities were measured on an automatic diffractometer and the atomic parameters obtained by direct phasing procedures and least-squares calculations. The derived molecular structure is shown in Figure 1 and the mean molecular dimensions are in Figure 2.

The N-C bond length in the azetidine ring, 1.403 Å, is rather longer than the corresponding distance in β-lactam rings, *e.g.* 1.382 Å in cephaloridine hydrochloride monohydrate,[7] and, conversely, the C=O distance in (4) 1.182 Å, is shorter than that in cephaloridine, 1.214 Å.[7] Since the N atom in (4) is conjugated with two carbonyl groups, these differences are not unexpected. The bond angles in the ring depart appreciably from 90°, the C-C-C angle of 83.6° being notably small.

The N atom in (4) is displaced by 0.04 Å from the plane of C(2), C(4), and C(5), whereas in β-lactams displacements of *ca.* 0.2 Å have been reported.[7] The atoms of the four-membered ring and the oxygen substituents are coplanar to within ±0.01 Å, but the N-CH₂ bond is bent slightly out of plane, with C(5) displaced by 0.08 Å from the ring plane. The out-of-plane distortions of an amide group can be partitioned between twisting around the C-N bond and out-of-plane bending at nitrogen and the carbonyl carbon.[8] The appropriate parameters [8] here have mean values of χ_N 5.1°, χ_c 0.8°, and τ 178.0° (*i.e.* a twist of 2°).

The absence of CO splitting in the infrared spectrum is consistent with the planarity of the azetidinedione system.
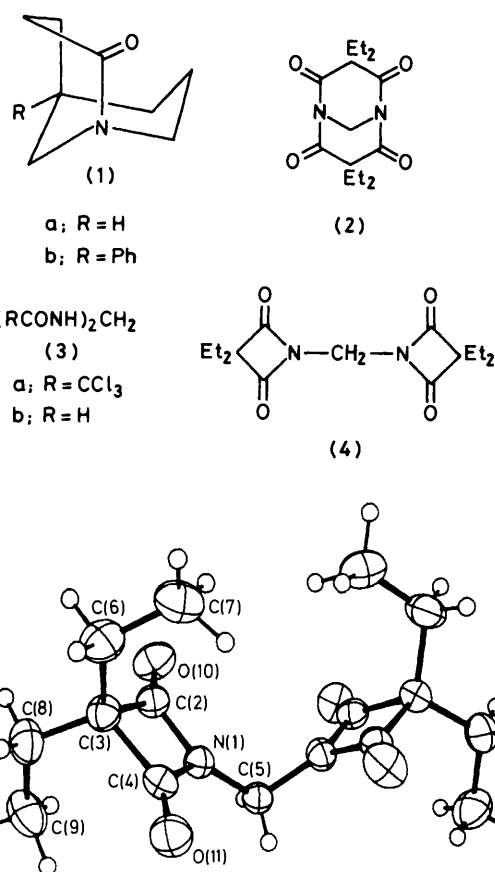

Figure 1. The molecular structure of the azetidinedione (4). The thermal ellipsoids of the C, N, and O atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0.1 Å

Experimental

Methylenebis(3,3-*diethylazetidine*-2,4-*dione*) (4).—Diethyl-malonic acid (2 g) in thionyl chloride (30 ml) was heated on the steam bath for 2 h, concentrated under reduced pressure, redissolved in a little dry benzene and reconcentrated. *N*,*N'*-Methylenebis(formamide) (1 g) was added to the oily residue and the mixture was shaken with sufficient dilute NaOH to maintain alkalinity and allowed to stand for 3 days. The alkaline solution was extracted with ether, washed and evaporated to yield a very small quantity of the azetidinedione, m.p.
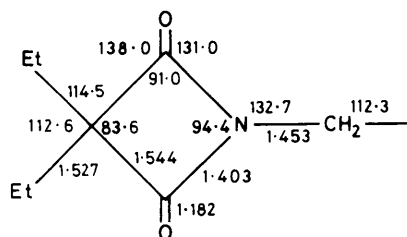
Figure 2. Dimensions of the molecule (average values). Bond lengths in Å, bond angles in degrees

Table 1. Fractional atomic co-ordinates

	x	y	z
N(1A)	0.582 6(2)	0.381 3(3)	0.052 4(1)
C(2A)	0.693 3(2)	0.283 0(4)	0.056 6(1)
C(3A)	0.705 6(2)	0.235 2(4)	0.131 8(1)
C(4A)	0.584 4(2)	0.347 9(3)	0.120 1(1)
C(5A)	0.500 0(—)	0.493 3(—)	0.000 0(—)
C(6A)	0.692 3(3)	0.030 7(4)	0.146 4(1)
C(7A)	0.592 3(3)	−0.071 0(5)	0.096 6(2)
C(8A)	0.819 3(3)	0.324 4(5)	0.181 4(1)
C(9A)	0.827 4(3)	0.530 7(5)	0.175 8(2)
O(10A)	0.748 3(2)	0.253 0(3)	0.015 6(1)
O(11A)	0.515 3(2)	0.396 6(3)	0.151 7(1)
N(1B)	0.029 8(2)	0.131 4(3)	0.447 6(1)
C(2B)	0.136 8(2)	0.032 3(3)	0.443 6(1)
C(3B)	0.074 2(2)	−0.014 2(4)	0.368 2(1)
C(4B)	−0.035 8(2)	0.099 0(4)	0.380 1(1)
C(5B)	0.000 0(—)	0.243 0(5)	0.500 0(—)
C(6B)	0.046 1(3)	−0.219 9(4)	0.353 8(1)
C(7B)	−0.004 5(3)	−0.321 1(5)	0.403 4(2)
C(8B)	0.138 2(3)	0.072 9(5)	0.318 9(1)
C(9B)	0.151 6(3)	0.281 9(5)	0.323 9(2)
O(10B)	0.232 8(2)	0.004 7(3)	0.484 5(1)
O(11B)	−0.136 2(2)	0.147 9(3)	0.384 6(1)

139 °C (benzene–ether) (Found: C, 61.35; H, 7.55; N, 9.5. $C_{15}H_{12}O_4N_2$ requires C, 61.22; H, 7.48; N, 9.52%); δ(C) 172.1 p.p.m. (CO); ν(CCl₄) 1 755 cm⁻¹ (CO).

Crystallographic Measurements.—Cell dimensions were derived from least-squares treatment of the setting angles of 25 reflections measured on an Enraf-Nonius CAD4 diffractometer with Mo-K_α radiation. For intensity measurements, reflections were surveyed in the range θ < 26°, and 1 540 satisfied the criterion $I > 2.5\sigma(I)$ and were used in the subsequent calculations.

Structure Analysis.—The crystal structure was elucidated with a direct-phasing program developed by Dr. C. J. Gilmore. The molecules were found to have crystallographic C_2 symmetry and the asymmetric unit comprises two independent half-molecules.

After preliminary adjustment of the positions of the C, N, and O atoms, the H atoms were located in a difference electron-density distribution. In the subsequent least-squares calculations, the co-ordinates of the H atoms were held constant and adjustment of the co-ordinates and anisotropic

* For details of the Supplementary Publications scheme, see Instructions to Authors (1983), *J. Chem. Soc., Perkin Trans. I*, 1983, Issue 1.

Table 2. Bond lengths (Å) and angles (°) for the azetidinedione (4)

N(1A)–C(2A)	1.401(4)	N(1B)–C(2B)	1.408(4)
N(1A)–C(4A)	1.403(3)	N(1B)–C(4B)	1.398(3)
N(1A)–C(5A)	1.455(2)	N(1B)–C(5B)	1.451(3)
C(2A)–C(3A)	1.549(4)	C(2B)–C(3B)	1.550(4)
C(2A)–O(10A)	1.183(3)	C(2B)–O(10B)	1.180(3)
C(3A)–C(4A)	1.535(4)	C(3B)–C(4B)	1.543(4)
C(3A)–C(6A)	1.525(5)	C(3B)–C(6B)	1.533(5)
C(3A)–C(8A)	1.532(4)	C(3B)–C(8B)	1.519(4)
C(4A)–O(11A)	1.183(3)	C(4B)–O(11B)	1.180(3)
C(6A)–C(7A)	1.484(5)	C(6B)–C(7B)	1.480(5)
C(8A)–C(9A)	1.502(6)	C(8B)–C(9B)	1.521(6)
C(4A)-N(1A)-C(2A)	94.3(2)	C(4B)-N(1B)-C(2B)	94.5(2)
C(5A)-N(1A)-C(2A)	134.0(2)	C(5B)-N(1B)-C(2B)	133.7(2)
C(5A)-N(1A)-C(4A)	131.5(2)	C(5B)-N(1B)-C(4B)	131.6(2)
C(3A)-C(2A)-N(1A)	90.8(2)	C(3B)-C(2B)-N(1B)	90.7(2)
O(10A)-C(2A)-N(1A)	131.4(3)	C(10B)-C(2B)-N(1B)	131.2(3)
O(10A)-C(2A)-C(3A)	137.8(3)	O(10B)-C(2B)-C(3B)	138.2(3)
C(4A)-C(3A)-C(2A)	83.6(2)	C(4B)-C(3B)-C(2B)	83.5(2)
C(6A)-C(3A)-C(2A)	115.2(3)	C(6B)-C(3B)-C(2B)	114.5(3)
C(8A)-C(3A)-C(2A)	113.6(3)	C(8B)-C(3B)-C(2B)	114.1(3)
C(6A)-C(3A)-C(4A)	114.8(3)	C(6B)-C(3B)-C(4B)	114.7(3)
C(8A)-C(3A)-C(4A)	114.1(3)	C(8B)-C(3B)-C(4B)	114.6(3)
C(8A)-C(3A)-C(6A)	112.7(3)	C(8B)—C(3B)-C(6B)	112.5(3)
C(3A)-C(4A)-N(1A)	91.3(2)	C(3B)-C(4B)-N(1B)	91.4(2)
O(11A)-C(4A)-N(1A)	130.7(3)	O(11B)-C(4B)-N(1B)	130.7(3)
O(11A)-C(4A)-C(3A)	138.0(3)	O(11B)-C(4B)-C(3B)	138.0(3)
N(1A)-C(5A)-N(1A')	112.3(3)	N(1B)-C(5B)-N(1B')	112.3(3)
C(7A)-C(6A)-C(3A)	116.2(3)	C(7B)-C(6B)-C(3B)	116.3(3)
C(9A)-C(8A)-C(3A)	115.1(3)	C(9B)-C(8B)-C(3B)	115.0(3)

thermal parameters of the C, N, and O atoms and the isotropic thermal parameters of the H atoms converged at $R = 0.040$, $R_w = 0.056$, with weights given by $w = 1/\sigma^2(F)$. These calculations were performed on a SEL 32/27 computer with an integrated system of programs developed by Drs. C. J. Gilmore, P. R. Mallinson, and K. W. Muir.

Atomic co-ordinates are listed in Table 1 and bond lengths and angles in Table 2. Observed and calculated structure amplitudes, thermal parameters, and hydrogen positions are listed in a Supplementary Publication (SUP No. 23526, 15 pages).*

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