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Laboratories, 1996). The structures of compounds similar to maleimide such as maleic anhydride (Marsh, Ubell & Wilcox, 1962) in which the endocyclic N atom is replaced by an O atom, and succinimide (Mason, 1961) in which the double bond is replaced by a single bond, were examined decades ago. However, X-ray analysis of maleimide required a low-temperature (150 K) study and rapid data collection to prevent decay of the crystal. In this study, the mosaicity of the crystal was also somewhat higher than normal (1.9° compared to 0.5–1.2°) and cell dimensions were obtained with some difficulty. Other triclinic and monoclinic cells derived from the experimental cell dimensions were examined with the program *LEPAGE* (Spek, 1988), but the experimental cell was the only one which resulted in a structure solution. Pseudosymmetry relating to a twofold axis is present between the atoms of molecules *A* and *D* and between those of *B* and *C*. This is shown by the average *y* coordinate of corresponding atom pairs which in each case is very close to 0.25.

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Maleimide

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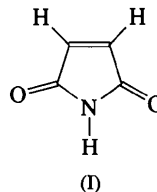
(Received 7 May 1996; accepted 23 May 1996)

Abstract

The triclinic unit cell of maleimide (1*H*-pyrrole-2,5-dione, C₄H₃NO₂), contains eight molecules which form four hydrogen-bonded dimers. Each dimer comprises a planar tricyclic ring system.

Comment

Maleimide, (I), is a reactive vinyl monomer used in free-radical-initiated polymerizations (Kirk–Othmer Encyclopaedia, 1983). A variety of polymers used for high-temperature aerospace applications are based on substituted cyclic five-membered imide rings. In particular, the polymer obtained from methylene dianiline bismaleimide is one of the most commonly used materials for these applications (Wilson, 1987). The maleimide group is also present in the antibiotic showdomycin (Neidle, Kaye & Reese, 1990) and antitumour activity has been shown by *N*-glycinylnmaleimide and its copolymers (Gam, Jeong, Lee, Ha & Cho, 1995). Maleimide compounds are also used in biochemical conjugations such as selective biotinylation of sulfhydryl (Dojindo



In the crystal, pairs of maleimide molecules are linked together to form planar tricyclic dimers (Fig. 1) by pairs of intermolecular N1—H···O1 hydrogen bonds. Molecule *A* links to molecule *C* and molecule *B* links to molecule *D*. The centre ring so formed contains eight atoms including the two H atoms. The dimers pack in sheets parallel to the *b* axis with the hydrogen bonding confined to each pair of dimers. In each molecule, the C—O bonds are longer where the O atom acts as an acceptor [C1—O1 range 1.214 (7)–1.235 (7) Å] than where it has no hydrogen-bonding role [C4—O2 range 1.190 (7)–1.221 (7) Å]. The O···N distances range from 2.851 (7)–2.917 (7) Å, the O···H distances from 1.98–2.05 Å and the N—H···O angles from 167–171°. (The N—H distances were fixed at 0.88 Å.) The C=C double bond [1.301 (8)–1.322 (8) Å] is normal and there is little evidence for any other tautomeric form. The diketo tautomer of maleimide has also been shown to be the most stable form in both the gas and solution phase (Acker, Hofmann & Cimraglia, 1994).

Each of the four molecules (including H atoms) is approximately planar with deviations of atoms from the mean least-squares planes ranging from –0.025 (4) to 0.025 (4) Å for *A*, –0.030 (4) to 0.033 (3) Å for *B*, –0.048 (3) to 0.055 (4) Å for *C* and –0.016 (3) to 0.016 (6) Å for *D*. The dimers are also somewhat planar with atom deviations from the best mean planes ranging from –0.145 (5) to 0.091 (5) Å for *A/C* and from –0.116 (5) to 0.100 (4) Å for *B/D*. The two dimers pack

parallel to each other, the angle between their respective mean planes being only 1.11 (15)°.

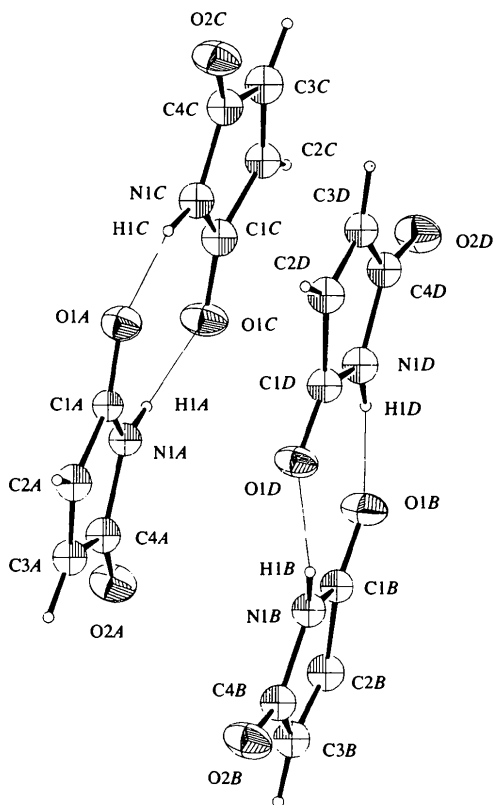


Fig. 1. The pair of maleimide dimers in the asymmetric unit showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are represented by small spheres of arbitrary radii.

Experimental

Maleimide was obtained from Aldrich Chemicals and recrystallized from acetone.

Crystal data

$C_4H_3NO_2$
 $M_r = 97.07$
 Triclinic
 $P\bar{1}$
 $a = 6.768 (12) \text{ \AA}$
 $b = 10.675 (14) \text{ \AA}$
 $c = 12.384 (12) \text{ \AA}$
 $\alpha = 81.37 (5)^\circ$
 $\beta = 77.01 (5)^\circ$
 $\gamma = 74.77 (12)^\circ$
 $V = 837 (2) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.540 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 250 reflections
 $\theta = 1.99\text{--}25.16^\circ$
 $\mu = 0.127 \text{ mm}^{-1}$
 $T = 150 (2) \text{ K}$
 Lozenge
 $0.20 \times 0.18 \times 0.16 \text{ mm}$
 Colourless

Data collection

Delft Instruments FAST diffractometer with CRYOSTREAM low-temperature attachment (Cosier & Glazer, 1986)
 Area detector scans
 Absorption correction: none
 3835 measured reflections

2253 independent reflections
 876 observed reflections
 $[I > 2\sigma(I)]$
 $R_{int} = 0.0881$
 $\theta_{max} = 25.16^\circ$
 $h = -7 \rightarrow 7$
 $k = -12 \rightarrow 7$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0630$
 $wR(F^2) = 0.1715$
 $S = 0.764$
 2250 reflections
 154 parameters
 H atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.0580P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.009$
 $\Delta\rho_{max} = 0.40 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.33 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*$ for O atoms, U_{iso} for others.

	x	y	z	U_{iso}/U_{eq}
O1A	-0.0995 (7)	0.3502 (3)	0.8594 (3)	0.0291 (11)
O2A	0.1138 (7)	0.0146 (4)	0.6421 (3)	0.0345 (13)
N1A	0.0249 (8)	0.2043 (4)	0.7261 (4)	0.0241 (13)
C1A	-0.0704 (10)	0.2394 (5)	0.8317 (5)	0.0216 (14)
C2A	-0.1225 (10)	0.1240 (5)	0.8977 (6)	0.030 (2)
C3A	-0.0647 (10)	0.0277 (5)	0.8356 (5)	0.027 (2)
C4A	0.0354 (10)	0.0714 (6)	0.7235 (6)	0.027 (2)
O1B	0.6025 (7)	0.1191 (3)	0.6459 (4)	0.0337 (12)
O2B	0.4130 (7)	-0.2269 (4)	0.8639 (4)	0.0374 (13)
N1B	0.4956 (8)	-0.0363 (4)	0.7790 (4)	0.0249 (13)
C1B	0.5785 (10)	0.0088 (5)	0.6752 (5)	0.0238 (15)
C2B	0.6310 (10)	-0.1030 (5)	0.6056 (6)	0.030 (2)
C3B	0.5747 (10)	-0.2026 (5)	0.6708 (5)	0.028 (2)
C4B	0.4841 (10)	-0.1652 (6)	0.7832 (5)	0.027 (2)
O1C	0.1847 (7)	0.3908 (3)	0.5596 (3)	0.0337 (12)
O2C	-0.0204 (7)	0.7264 (4)	0.7791 (4)	0.0379 (13)
N1C	0.0513 (8)	0.5403 (4)	0.6904 (4)	0.0280 (14)
C1C	0.1585 (10)	0.5004 (5)	0.5889 (5)	0.029 (2)
C2C	0.2293 (10)	0.6153 (5)	0.5236 (5)	0.027 (2)
C3C	0.1654 (10)	0.7124 (6)	0.5864 (5)	0.031 (2)
C4C	0.0555 (10)	0.6689 (6)	0.6958 (6)	0.029 (2)
O1D	0.3220 (7)	0.1502 (3)	0.9455 (3)	0.0288 (12)
O2D	0.5291 (7)	0.4913 (4)	0.7226 (4)	0.0356 (13)
N1D	0.4491 (8)	0.2998 (4)	0.8104 (4)	0.0290 (13)
C1D	0.3476 (10)	0.2595 (6)	0.9160 (5)	0.026 (2)
C2D	0.2758 (10)	0.3770 (5)	0.9775 (5)	0.029 (2)
C3D	0.3360 (9)	0.4753 (5)	0.9119 (5)	0.0254 (15)
C4D	0.4480 (10)	0.4327 (6)	0.8044 (5)	0.026 (2)

Table 2. Comparison of molecular geometry parameters (\AA , $^\circ$) for the four molecules in the asymmetric unit

Parameter	Molecule A	Molecule B	Molecule C	Molecule D
O1—C1	1.235 (7)	1.221 (7)	1.234 (7)	1.214 (7)
O2—C4	1.200 (7)	1.190 (7)	1.221 (7)	1.207 (7)
N1—C1	1.381 (7)	1.352 (7)	1.370 (8)	1.396 (7)
N1—C4	1.407 (7)	1.391 (7)	1.392 (8)	1.408 (8)
C1—C2	1.452 (8)	1.497 (8)	1.492 (8)	1.480 (8)
C2—C3	1.301 (8)	1.321 (8)	1.321 (8)	1.322 (8)
C3—C4	1.466 (9)	1.458 (9)	1.464 (9)	1.450 (9)

C1—N1—C4	108.8 (5)	111.4 (5)	109.9 (5)	109.8 (5)
O1—C1—N1	123.6 (5)	126.1 (6)	125.3 (6)	124.9 (6)
O1—C1—C2	129.3 (6)	127.9 (6)	128.4 (6)	129.5 (6)
N1—C1—C2	107.1 (5)	106.1 (5)	106.4 (5)	105.6 (5)
C3—C2—C1	109.1 (6)	107.3 (6)	108.0 (6)	108.6 (6)
C2—C3—C4	109.6 (6)	110.1 (6)	109.5 (6)	110.2 (6)
O2—C4—N1	123.0 (6)	124.9 (6)	123.3 (6)	123.3 (6)
O2—C4—C3	131.7 (6)	129.9 (6)	130.5 (6)	130.9 (6)
N1—C4—C3	105.4 (5)	105.2 (5)	106.2 (6)	105.8 (5)

The unit-cell and intensity data were collected on a Delft Instruments FAST diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989) and processed using *ABSMAD* (Karaulov, 1992); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). Owing to the small number of observed reflections, only the O atoms were refined with anisotropic displacement parameters. The absence of crystal decay in the X-ray beam was confirmed by checking equivalent reflections at the beginning and end of data collection which lasted about 8 h. Refinement was on F^2 for all reflections except for three which had very negative F^2 or were flagged by the user for potential systematic errors.

The H atoms were initially placed in calculated positions and thereafter allowed to ride on their attached C atoms with a common isotropic displacement parameter of 0.044 (5) Å².

Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL93*.

The recrystallization of maleimide by A. J. Florence and the use of the EPSRC X-ray Crystallographic Service at the University of Wales, Cardiff are gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trimethylsulfonium Bromide

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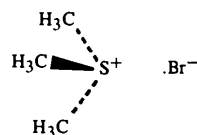
(Received 7 February 1996; accepted 17 May 1996)

Abstract

The reaction of dimethyl sulfoxide and ethyl bromoacetate at room temperature gives the title compound (CH₃)₃S⁺Br⁻, which consists of layers of pyramidal trimethylsulfonium ions and bromide ions.

Comment

Vibrational spectra of (CH₃)₃S⁺3I⁻ (*I*) and (C₂H₅)₃S⁺3I⁻ (*I*) have been shown (Bengtsson, Oskarsson, Stegemann & Redeker, 1994; Bengtsson, Stegemann, Holmberg & Füllbier, 1991) to have extra spectral features in the region of 130–170 cm⁻¹ which are unexpected since the triiodide ions in these compounds have *D_{3h}* symmetry. An ion of *C_{3v}* symmetry could provide essential information for the further elucidation of the reasons for the breakdown of selection rules. This is not possible in the liquid state if only iodine is present in the linear triatomic ion but if one of the terminal I atoms is replaced by another halogen atom, *C_{3v}* symmetry is obtained. The title compound was found to be a suitable starting material to form linear I₂Br⁻ (Svensson & Kloo, 1996). The structure of the title compound has been determined in order to obtain data for future comparisons.



(I)