NEWTON, M. G., BROWN, H. C., FINDER, C. J., ROBERT, J. B., MARTIN, J. & TRANQUI, D. (1974). *J. Chem. Soc. Chem. Commun.* pp. 455–456.

PAPPALARDO, G. C., CHAKRAVORTY, R., IRGOLIC, K. J. & MEYERS, E. A. (1983). *Acta Cryst.* C39, 1618–1620.

SCHULTZ, G. Y., HARGITTAI, I., MARTIN, J. & ROBERT, J. B. (1974). *Tetrahedron,* 30, 2365–2369.

TUZOVA, L. L., NAUMOV, V. A., GALIAKBEROV, R. M., OFITSEROV, E. N. & PUDOVIK, A. N. (1981). *Dokl. Akad. Nauk SSSR,* 256, 891–894.

Structure of Methylenecyclopropane-2-carboxamide* by Time-of-Flight Neutron Diffraction

By ARTHUR J. SCHULTZ

Chemistry and Materials Science Divisions, Argonne National Laboratory, Argonne, Illinois 60439, USA

DONALD G. VAN DERVEER

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA

DAVID W. PARKER

Department of Chemistry, University of Oregon, Eugene, Oregon 97403, USA

AND JOHN E. BALDWIN

Department of Chemistry, Syracuse University, Syracuse, New York 13244, USA

Abstract. C_5H_7NO, $M_r = 97.1$, monoclinic, $P2_1/c$, $a = 7.181$ (3), $b = 15.495$ (5), $c = 8.995$ (2) Å, $\beta = 104.89$ (2)°, $V = 967.2$ (5) Å^3, $Z = 8$, $D_x = 1.33$ Mg m^{-3}, time-of-flight neutron diffraction, $\lambda = 0.7$ to 4.2 Å, $\mu = 1.98$ to 5.90 cm^{-1}, $T = 20$ K, $R(F) = 0.064$, $wR(F^2) = 0.119$ for 3150 reflections ($F_o{}^2 > 3\sigma$). The asymmetric unit contains two independent, but nearly identical, neutral molecules. The orientation of the exocyclic methylene group with respect to the carboxamide group is consistent with stereochemical preferences shown by methylenecyclopropane rearrangements.

Introduction. The stereochemical preferences exhibited by the [1,3] sigmatropic carbon shift in the methylenecyclopropane rearrangement, (1)→(2), a reaction that continues to attract serious theoretical scrutiny (Skancke, Schaad & Hess, 1988), are not entirely understood. A single-crystal X-ray structure determination of methylenecyclopropane-2-carboxamide revealed a displacement of the exocyclic methylene carbon C(4) toward the carboxamide-substituted ring carbon C(2), which is the preferred pivot atom in the methylenecyclopropane rearrangement (Van Derveer, Baldwin & Parker,

1987). We have undertaken a neutron diffraction investigation in order to locate precisely the hydrogen atoms and fully characterize the molecular geometry.
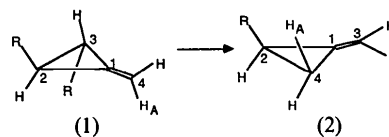
Experimental. Time-of-flight (TOF) neutron diffraction data were obtained at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory using the single-crystal diffractometer equipped with an area position-sensitive ^{6}Li-glass scintillation detector and an Air Products Displex closed-cycle helium refrigerator for cooling the sample (Schultz, 1987). A $0.6 \times 1.6 \times 2.2$ mm crystal, obtained by very slow concentration through evaporation of a benzene solution of the amide, was maintained at a temperature of 20 K. 24 crystal orientations were required to cover a unique quadrant of reciprocal space. For each crystal setting, data were stored in three-dimensional histogram form with coordinates x, y, t corresponding to horizontal and vertical detector positions and the TOF, respectively. The 120 TOF histogram channels were constructed with

---

constant $\Delta t/t = 0\cdot015$ and correspond to wavelengths of $0\cdot7$ to $4\cdot2$ Å. The area detector, with nominal dimensions of 28×28 cm, was centered at $2\theta = 90°$ at a distance of 32 cm from the crystal. Thus, a complete shell out to $(\sin\ \theta)/\lambda = 0\cdot98$ Å^{-1} was obtained with additional data extending to a maximum of $1\cdot16$ Å^{-1}.

Initially, an orientation matrix was obtained by an autoindexing procedure (Jacobson, 1986) using data obtained by searching a histogram for peaks. Bragg reflections were integrated about their predicted histogram location and were corrected for the Lorentz factor, the incident spectrum, the detector efficiency, dead-time losses and crystal absorption. The linear absorption coefficients, calculated from the incoherent and absorption cross sections (Howard, Johnson, Schultz & Stringer, 1987; Sears, 1986), are $\mu = 1\cdot98$ cm^{-1} at $\lambda = 0\cdot7$ Å and $\mu = 5\cdot90$ cm^{-1} at $\lambda = 4\cdot2$ Å. For reflections with wavelengths between the two end points, μ was determined by a simple interpolation which is valid in the absence of nuclear resonances for all the elements in the crystal. Final unit-cell parameters were obtained from a least-squares refinement of the observed centroid positions of the 768 strongest reflections from all the data.

The initial coordinates for the non-hydrogen atoms were those from the X-ray structure (Van Derveer, Baldwin & Parker, 1987). Hydrogen atoms were located in a difference Fourier map using phases calculated from the non-hydrogen atomic coordinates. 3150 data $(F_o^2 > 3\sigma)$, $h - 4{\rightarrow}15$, $k - 7{\rightarrow}20$, $l - 17{\rightarrow}18$. Atomic scattering lengths used in the least-squares refinements were those tabulated by Sears (1986): b(H) $= -3\cdot739$, b(C) $= 6\cdot646$, b(N) $= 9\cdot36$, b(O) $= 5\cdot803$ fm. Function minimized was $\Sigma w(F_{obs}^2 - F_{calc}^2)^2$ where $w = 1/\sigma(F_{obs}^2)$ and $\sigma(F_{obs}^2) = [\sigma_{counting}^2 + (0\cdot03F_{obs}^2)]^{1/2}$. In the final cycles of least-squares refinements all atoms were treated with anisotropic temperatures factors. $\Delta/\sigma = 1\cdot4 \times 10^{-4}$, $S = 1\cdot55$. A correction for type I secondary extinction with a Lorentzian distribution (Becker & Coppens, 1974a,b, 1975; Jauch, Schultz & Schneider, 1988) was included, with $g = 0\cdot181$ (9) $\times 10^{-4}$ and a minimum extinction factor y of $0\cdot56$. The largest positive and negative peaks from a final difference Fourier synthesis are $0\cdot166$ and $-0\cdot161$ fm Å^{-3}. The atomic positional and equivalent isotropic thermal parameters are given in Table 1.*

Discussion. Fig. 1 is a stereoview of the unit-cell packing including N—H$\cdots$O hydrogen-bonding

---

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters for methylenecyclopropane-2-carboxamide at 20 K from neutron diffraction data*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
C(1A)	0·0999 (2)	0·1622 (1)	0·1213 (2)	0·0145 (5)
C(2A)	0·0181 (3)	0·2226 (1)	0·2138 (2)	0·0150 (5)
C(3A)	0·2342 (2)	0·2097 (1)	0·2397 (2)	0·0159 (5)
C(4A)	0·0630 (2)	0·1056 (2)	0·0083 (2)	0·0178 (5)
C(5A)	−0·0728 (2)	0·1844 (1)	0·3300 (2)	0·0123 (4)
O(A)	0·0052 (3)	0·1254 (2)	0·4157 (3)	0·0170 (6)
N(A)	−0·2412 (2)	0·2162 (1)	0·3346 (1)	0·0148 (3)
C(1B)	0·5084 (2)	−0·0825 (1)	0·1427 (2)	0·0140 (5)
C(2B)	0·4405 (2)	−0·0304 (1)	0·2556 (2)	0·0131 (5)
C(3B)	0·6524 (2)	−0·0514 (1)	0·2730 (2)	0·0160 (5)
C(4B)	0·4573 (2)	−0·1302 (2)	0·0171 (2)	0·0172 (5)
C(5B)	0·3409 (2)	−0·0772 (1)	0·3569 (2)	0·0120 (4)
O(B)	0·3896 (3)	−0·1512 (2)	0·4040 (2)	0·0147 (5)
N(B)	0·1947 (2)	−0·0367 (1)	0·3900 (2)	0·0154 (4)
H(1A)	−0·0434 (6)	0·2818 (3)	0·1595 (5)	0·030 (1)
H(2A)	0·3126 (7)	0·2621 (4)	0·2060 (6)	0·035 (1)
H(3A)	0·3042 (6)	0·1767 (4)	0·3455 (5)	0·033 (1)
H(4A)	−0·0808 (6)	0·0922 (4)	−0·0523 (6)	0·039 (2)
H(5A)	0·1764 (6)	0·0722 (4)	−0·0260 (6)	0·037 (2)
H(6A)	−0·3043 (6)	0·1940 (3)	0·4164 (5)	0·028 (1)
H(7A)	−0·3023 (6)	0·2643 (3)	0·2626 (5)	0·028 (1)
H(1B)	0·3954 (6)	0·0347 (3)	0·2251 (6)	0·029 (1)
H(2B)	0·7404 (7)	0·0026 (4)	0·2575 (6)	0·038 (2)
H(3B)	0·7173 (6)	−0·0950 (4)	0·3630 (5)	0·032 (1)
H(4B)	0·3112 (6)	−0·1370 (4)	−0·0426 (5)	0·036 (1)
H(5B)	0·5613 (7)	−0·1651 (4)	−0·0272 (6)	0·037 (2)
H(6B)	0·1222 (6)	−0·0674 (3)	0·4598 (5)	0·026 (1)
H(7B)	0·1612 (6)	0·0245 (3)	0·3596 (6)	0·029 (1)

interactions. Cooling from room temperature (Van Derveer, Baldwin & Parker, 1987) to 20 K produces a $7\cdot3$% reduction of the unit-cell volume due to contraction of a, b and c by $3\cdot2$, $2\cdot8$ and $1\cdot1$%, respectively. The atom-labeling scheme is shown in Fig. 2. The bond distances and angles given in Table 2 verify that the two independent molecules, labeled A and B, have similar geometries. Distances and angles, at room temperature, for the non-hydrogen atoms, derived from X-ray data are nearly identical to those obtained at 20 K with neutron data. The largest difference is in the C(2)—C(3) distance for molecule A [molecule B], which is $1\cdot545$ (3) Å [$1\cdot551$ (4) Å] at room temperature and $1\cdot522$ (3) Å [$1\cdot524$ (3) Å] at 20 K. This difference is not readily explainable since the change is opposite to the expected effect of apparent bond shortening at higher temperatures due to greater rigid body thermal librations.

The distortions of the methylenecyclopropane skeleton from idealized C_{2v} geometry observed in the X-ray structure (Van Derveer, Baldwin & Parker, 1987) are confirmed with the low-temperature neutron diffraction data. The displacement of the C(4) methylene group toward C(2) for molecule A [molecule B] produces nonequivalent C(3)—C(1)—C(4) and C(2)—C(1)—C(4) angles of $146\cdot1$ (2) [$145\cdot8$ (2)] and $150\cdot9$ (2)° [$150\cdot6$ (2)°], respectively. In addition,

the longest C—C distance in the cyclopropane ring is C(3)—C(2) = 1·522 (3) Å [1·524 (3) Å] and the shortest is C(3)—C(1) = 1·441 (3) Å [1·433 (3) Å]. This geometry appears to be consistent with a rearrangement involving formation of a C(2)—C(4) bond, breaking of the C(2)—C(3) bond and increasing the C(1)—C(3) bond order from 1 to 2. The distortions from idealized geometry provide strong evidence for ground-state 'orbital distortions' which correlate with the stereochemical course of methylenecyclopropane rearrangements (Burgess & Liotta, 1981).

The dihedral angles between the C(1)—C(2)—C(3) and the H(4)—C(4)—H(5) planes are slightly different for molecules A and B, with values of 1·0 (4) and 4·9 (5)°, respectively. That is, the C(4) methylene group of molecule A is statistically in the plane of the cyclopropane carbon atoms. In the case of molecule B, the H(4)—C(4)—H(5) plane is tilted out of the C(1)—C(2)—C(3) plane in the direction of the carboxamide group, as shown in Fig. 3. Based on preliminary analyses, it was previously reported (Van Derveer, Baldwin & Parker, 1987) that the H(4)—C(4)—H(5) plane is also slightly twisted about the C(1)—C(4) vector such that one of the diastereotopic faces of the C(4) methylene group appears to be oriented more favorably for bonding to C(2). The results of the current analysis are that the H(4) and
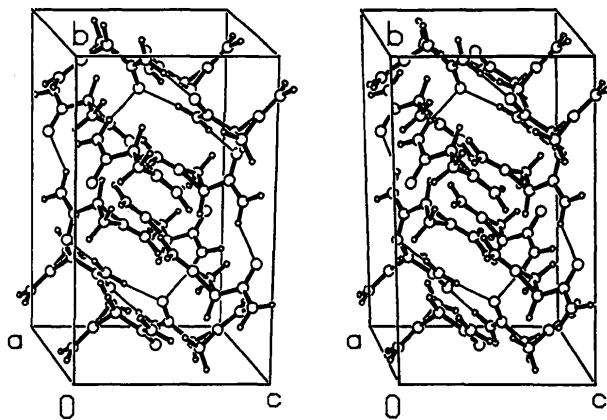
Table 2. *Selected interatomic distances (Å), angles (°) and hydrogen bonds (Å)*

C(1A)—C(2A)	1·471 (3)	C(1B)—C(2B)	1·475 (3)
C(1A)—C(3A)	1·441 (3)	C(1B)—C(3B)	1·433 (3)
C(1A)—C(4A)	1·317 (3)	C(1B)—C(4B)	1·320 (3)
C(2A)—C(3A)	1·522 (3)	C(2B)—C(3B)	1·524 (3)
C(2A)—C(5A)	1·489 (3)	C(2B)—C(5B)	1·484 (3)
C(2A)—H(1A)	1·079 (5)	C(2B)—H(1B)	1·073 (5)
C(3A)—H(2A)	1·075 (6)	C(3B)—H(2B)	1·079 (6)
C(3A)—H(3A)	1·083 (5)	C(3B)—H(3B)	1·066 (5)
C(4A)—H(4A)	1·057 (5)	C(4B)—H(4B)	1·054 (5)
C(4A)—H(5A)	1·074 (5)	C(4B)—H(5B)	1·079 (5)
C(5A)—O(A)	1·234 (3)	C(5B)—O(B)	1·241 (3)
C(5A)—N(A)	1·316 (2)	C(5B)—N(B)	1·322 (2)
N(A)—H(6A)	1·018 (5)	N(B)—H(6B)	1·030 (4)
N(A)—H(7A)	1·011 (5)	N(B)—H(7B)	0·999 (5)
C(2A)—C(1A)—C(3A)	63·0 (1)	C(2B)—C(1B)—C(3B)	63·2 (1)
C(2A)—C(1A)—C(4A)	146·1 (2)	C(2B)—C(1B)—C(4B)	145·8 (2)
C(3A)—C(1A)—C(4A)	150·9 (2)	C(3B)—C(1B)—C(4B)	150·6 (2)
C(1A)—C(2A)—C(3A)	57·5 (1)	C(1B)—C(2B)—C(3B)	57·1 (1)
C(1A)—C(2A)—C(5A)	117·0 (2)	C(1B)—C(2B)—C(5B)	116·9 (2)
C(3A)—C(2A)—C(5A)	117·0 (2)	C(3B)—C(2B)—C(5B)	117·3 (2)
C(1A)—C(3A)—C(2A)	59·5 (1)	C(1B)—C(3B)—C(2B)	59·7 (1)
C(2A)—C(5A)—O(A)	121·5 (2)	C(2B)—C(5B)—O(B)	121·5 (2)
C(2A)—C(5A)—N(A)	116·5 (2)	C(2B)—C(5B)—N(B)	116·2 (2)
O(A)—C(5A)—N(A)	122·0 (2)	O(B)—C(5B)—N(B)	122·2 (2)
H(6A)···O(B^i)	1·984 (5)	H(6B)···O(A^i)	1·851 (4)
H(7A)···O(B^ii)	1·968 (5)	H(7B)···O(A)	2·060 (5)

Symmetry operation applied to coordinates in Table 1: (i) $-x$, $-y$, $1-z$; (ii) $-x$, $0·5+y$, $0·5-z$.

Fig. 3. Nonperspective view of molecule B drawn with arbitrary ellipsoids. C(3) is hidden from view behind C(2). Note the upward tilt of the C(4) methylene group out of the cyclopropane ring plane.

Fig. 1. Stereoview of the unit cell. Atoms are drawn with arbitrary ellipsoid sizes. N—H···O hydrogen bonds are shown as thin lines.

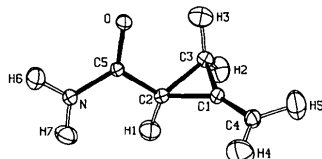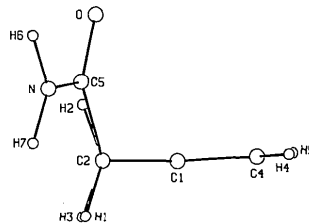Fig. 2. Perspective drawing of molecule A showing atom-labeling scheme for molecules A and B. Thermal ellipsoids are shown at the 50% probability level.

H(5) atoms are −0·021 [0·118] and 0·005 Å [0·137 Å], respectively, from the C(1)—C(2)—C(3) plane, with estimated standard deviations of ± 0·005 Å, where a positive displacement is towards the carboxamide group in Fig. 3. Thus, the evidence for rotation of the C(4) methylene about the C(1)—C(4) vector is not statistically significant. The same conclusion is arrived at upon examination of the torsion angles of C(2)—C(1)—C(4)—H(4) = 0·9 (7) [4·7 (7)], C(3)—C(1)—C(4)—H(5) = 0·7 (7) [−4·8 (7)], C(2)—C(1)—C(4)—H(5) = −179·6 (7) [−173·5 (5)] and C(3)—C(1)—C(4)—H(4) = −178·7 (5)° [173·5 (5)°]. For molecule A, the angles are statistically equivalent to 0 or 180°, whereas for molecule B, the C(2)—C(1)—C(4)—H(4) and C(2)—C(1)—C(4)—H(5) angles have the same magnitudes but opposite signs of the C(3)—C(1)—C(4)—H(5) and C(3)—C(1)—C(4)—H(4) angles,

respectively, indicating the absence of rotation about the C(1)—C(4) bond.

References

BECKER, P. J. & COPPENS, P. (1974a). *Acta Cryst.* A30, 129–147.
BECKER, P. J. & COPPENS, P. (1974b). *Acta Cryst.* A30, 148–153.
BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* A31, 417–425.
BURGESS, E. M. & LIOTTA, C. L. (1981). *J. Org. Chem.* **46**, 1703–1708.
HOWARD, J. A. K., JOHNSON, O., SCHULTZ, A. J. & STRINGER, A. M. (1987). *J. Appl. Cryst.* **20**, 120–122.
JACOBSON, R. A. (1986). *J. Appl. Cryst.* **19**, 283–286.
JAUCH, W., SCHULTZ, A. J. & SCHNEIDER, J. R. (1988). *J. Appl. Cryst.* **21**, 975–979.
SCHULTZ. A. J. (1987). *Trans. Am. Crystallogr. Assoc.* **23**, 61–69.
SEARS, V. F. (1986). *Methods of Experimental Physics,* edited by K. SKÖLD & D. L. PRICE, Vol. 23, Part A, pp. 521–550. Orlando: Academic Press.
SKANCKE, A., SCHAAD, L. J. & HESS, B. A. JR (1988). *J. Am. Chem. Soc.* **110**, 5315–5316.
VAN DERVEER, D. G., BALDWIN, J. E. & PARKER, D. W. (1987). *J. Org. Chem.* **52**, 1173–1174.

(Z)-Methyl 2-Phenyl-2-(pyrid-4-yl)vinyl Sulfoxide

BY M. MADESCLAIRE,* J. METIN AND D. ROCHE

Laboratoire de Chimie Pharmaceutique, UFR de Pharmacie, Université de Clermont-Ferrand I, BP 38, 63001 Clermont-Ferrand CEDEX, France

AND A. FAUVE

Laboratoire de Chimie Organique Biologique, UA 485 CNRS, Université Blaise Pascal, 63177 Aubière CEDEX, France

Abstract. $C_{14}H_{13}NOS$, $M_r = 243·33$, triclinic, $P\bar{1}$, $a = 5·455$ (6), $b = 10·064$ (3), $c = 12·831$ (1) Å, $\alpha = 71·59$ (3), $\beta = 79·60$ (7), $\gamma = 75·79$ (5)°, $V = 643·8$ Å³, $Z = 2$, $D_m = 1·27$, $D_x = 1·26$ g cm⁻³, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 2·3$ cm⁻¹, $T = 293$ K, final $R = 0·047$ for 2369 observed reflections (of 8164 unique data). For the title compound the unambiguous identification of the Z configuration by X-ray diffraction confirms a previous tentative assignment based on NMR. The two planar rings (phenyl and pyridyl) are at an angle of about 87°. Crystal cohesion is ensured by a dense network of van der Waals contacts.

Introduction. Certain unsaturated sulfoxides and particularly vinyl sulfoxides have been found to have a significant antianoxia activity (Madesclaire, Roche, Carpy & Boucherle, 1982).

Knowledge of the exact configuration of the Z and E diastereoisomers was required in order to perform a pharmacological study and to establish any structure–activity relationships. The stereoisomers were prepared by oxidation of sulfides with *m*-chloroperbenzoic acid (*m*-CPBA) (Madesclaire,

1986). The vinyl sulfides were synthesized by the Horner–Wittig reaction and separated by flash chromatography (Roche, Madesclaire, Veschambre & Fauve, 1988).

Experimental. Plate-like crystals of the title compound were grown by slow evaporation (a few weeks) of an ether solution at 277 K. D_m by flotation; white crystal, dimensions $0·75 \times 0·55 \times 0·07$ mm; unit-cell parameters using 24 reflections with θ values of about 10° and refining by the least-squares method; data collection on Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan mode, θ scan width $(1·0 + 0·35\tan\theta)°$, aperture width $(2·0 + 1·0\tan\theta)$ mm; data having $2\theta_{max} \le 80°$, $-9 \le h \le 9$, $-18 \le k \le 18$, $0 \le l \le 23$ measured; intensities of three standard reflections monitored after every 3600 s of exposure; variation in intensity $\le 2\%$ during complete data collection; orientation matrix checked every 100 reflections, no significant systematic fluctuation; 8164 reflections registered and reduced to 2369 with $I \ge 3\sigma(I)$; intensities corrected for Lorentz and polarization effects but not for absorption; structure solved using *MULTAN*11/82

---

* To whom correspondence should be addressed.