Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Experimental electron density study of ethylene oxide at 100 K

Simon Grabowsky, Manuela Weber, Jürgen Buschmann and Peter Luger*

Institut für Chemie und Biochemie/Kristallographie, Freie Universität Berlin, Fabeckstrasse 36a, D-14195 Berlin, Germany

Correspondence e-mail: luger@chemie.fu-berlin.de

Received 18 February 08
Accepted 14 April 08

The experimental electron density of ethylene oxide was derived from a multipole refinement of 100 K X-ray data and complemented by density-functional calculations at experimental and optimized geometry. Atomic and bond-topological properties were derived using the atoms-in-molecules (AIM) formalism. The high strain in the three-membered ring molecule is mainly expressed by the high ellipticities of the three bonds in this ring, while the bond paths are only slightly bent for the C—C bond, but are virtually straight for the C—O bond.

1. Introduction

The X-ray structure of ethylene oxide (oxirane) which is gaseous at room temperature and melts at 161 K was examined more than 20 years ago. Based on a low-resolution X-ray data set measured with Cu $K\alpha$ radiation at $T = 150$ K, the spherical structure was determined showing the molecule to be an almost equilateral triangle with equal C—O and C—C distances (Luger *et al.*, 1986). Here we report on the electron-density (ED) distribution obtained from a high-resolution Mo $K\alpha$ dataset at $T = 100$ K and on the results of a topological analysis after Bader's QTAIM formalism yielding quantitative atomic and bond-topological properties (Bader, 1994).

2. Experimental and multipole refinement calculations

Commercially available ethylene oxide was crystallized *in situ* on a Stoe four-circle diffractometer following a method described earlier (Luger & Buschmann, 1983, 1984). Intensity data of 4382 reflections were collected at 100 K (N_2-gas stream cooling) using Mo $K\alpha$ radiation (graphite monochromator) and a scintillation counter. Further details of the crystal data and the experimental conditions are given in Table 1.[1]

An independent dataset obtained from the merging routine implemented in *SHELXL*97 (Sheldrick, 2008) and the spherical model were entered into a multipole refinement (Hansen & Coppens, 1978) using the corresponding software of the program package *XD* (Volkov *et al.*, 2006). In addition to positional parameters, anisotropic displacement parameters were refined for C and O atoms, but were fixed for H atoms as obtained from the program *SHADE* (Madsen, 2006). Multipole populations up to hexadecapolar level for C and O atoms, and bond-directed dipoles for H atoms were also refined. Local m symmetry was imposed on the two C atoms, whereas no symmetry was applied to the oxygen because it is involved in non-symmetric intermolecular C—H$\cdots$O interactions (see below). For the same reason the four H atoms were not considered equivalent, but the two C atoms were constrained to each other. C—H distances were fixed to neutron values (1.10 Å; Allen *et al.*, 1992). κ and κ' parameters were refined for C and O atoms, but kept at $\kappa = 1.13$ and $\kappa' = 1.29$ for H atoms (Volkov *et al.*, 2001). After convergence, the residual electron density was practically featureless ($\Delta\rho_{\min}/\Delta\rho_{\max} = -0.14/0.16$ e Å^{-3}), the Hirshfeld rigid-bond test (Hirshfeld, 1976) was

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS5059). Services for accessing these data are described at the back of the journal.

doi:10.1107/S0108768108010197

Table 1
Crystal and structure refinement data for ethylene oxide at 100 K.

Crystal data	
Chemical formula	C_2H_4O
M_r	44.05
Cell setting, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	4.633 (5), 8.400 (1), 6.577 (3)
β (°)	100.37 (6)
V (Å^3)	251.8 (3)
Z	4
D_x (Mg m^{-3})	1.162
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.09
$F(000)$	96
Crystal form, color	Endless cylinder, colorless,
Crystal size	0.3 mm diameter
Data collection	
Diffractometer	Point detector
Data collection method	φ scans
Absorption correction	None
No. of measured, independent and observed reflections	4382, 2081, 1424
Criterion for observed reflections	$I > 3\sigma(I)$
$R_{\rm int}$	0.029
$\theta_{\rm max}$ (°)	45.0
No. and frequency of standard reflections	3 every 60 min
Multipole refinement	
Refinement on	F
$R[F > 3\sigma(F)]$, $wR(F^2)$, S	0.030, 0.046, 1.33
No. of reflections	1424
No. of parameters	79
Weighting scheme	$w1 = 1/\sigma^2(F_o)$
Overall completeness (%)	100
Redundancy	2.1
$(\Delta/\sigma)_{\rm max}$	< 0.0001
$\Delta\rho_{\rm max}$, $\Delta\rho_{\rm min}$ (e Å^{-3})	0.16, −0.14

Computer programs used: *SHELXL*97 (Sheldrick, 2008), *XD* (Volkov *et al.*, 2006).

satisfied, and the mean-square atomic displacements were smaller than 0.001 Å^2 for all bonds. For further refinement details see also Table 1.

3. Results and discussion

Compared with the 150 K structure from an independent atom model treatment the C—O and C—C bonds have become longer by 0.006–0.007 and 0.019 Å, respectively, so that there is a small difference of *ca* 0.02 Å between the C—C distance and the average of the two C—O bond lengths. In the crystal lattice three C—H⋯O contacts exist (see Table 2), which cause small asymmetries in the electron-density distribution.

Bond-topological and atomic properties are summarized in Table 2 and Fig. 1, respectively. Owing to the high strain in the three-membered ring the bond paths in the ring could be expected to be longer than the internuclear vectors. This is not really seen for the C—O bonds, but for the C—C bond the bond path is 0.008 Å longer than the direct C—C distance. A comparable small difference between bond path and internuclear vector was found in the cyclopropane ring of bullvalene (Koritsánszky *et al.*, 1996), a barbaralane derivative (Scheins, 2002) and some cyclopropane-ring-containing opioids (Scheins *et al.*, 2007).

The topological properties on the bond-critical points (b.c.p.'s) can be summarized as follows: For the C—O bonds, which are comparable in length to bonds in C—O—C sequences in carbohydrates (1.43–1.44 Å), the values of the electron densities ρ(b.c.p.) agree with those found for sucrose, which was recently the subject of a charge-density study (Jaradat *et al.*, 2007).

The C—C bond shows unexpected properties in that it is on one hand significantly shorter than a C—C single bond, but has on the other hand an ED at the b.c.p. [1.72 (1) e Å^{-3}], which agrees with the corresponding values of pure C—C single bonds [sucrose: average of ten C—C single bonds: ρ(b.c.p.) = 1.76 (1) e Å^{-3}, five opioids: average of 93 C—C single bonds: ρ(b.c.p.) = 1.68 (7) e Å^{-3}]. Common to the three covalent bonds in the ring are the large ellipticities which were, for example, also found in the cyclopropane ring in bullvalene and the above-mentioned opioid derivatives. It indicates a delocalization of density into the interior of the ring, which is also expressed by the relatively high ED of 1.42 e Å^{-3} at the ring critical point. For comparison, this value is much smaller in the furanosyl/pyranosyl rings of sucrose (0.24/0.14 e Å^{-3}) because in the larger five- and six-membered rings the atoms are much farther apart from the ring-critical point.

Atomic properties (V_{001}/q_{001}, Fig. 1*b*) show no unusual behavior. The volume of the oxygen is *ca* 3 Å^3 larger than the ether O atoms in the furanosyl/pyranosyl rings of sucrose, the charge is ~ 0.2 e less negative than for the corresponding sucrose O atoms. The C-atom volumes, which are larger than 10 Å^3 may be compared with the methoxy C atoms in sucrose having the same next-nearest neighbors (but in different geometry) or with C atoms in cyclopropane rings. Cyclopropane C atoms are comparable in volume, methoxy C atoms in sucrose have somewhat smaller volumes (7.5–8.3 Å^3). No significant differences in the slightly positive charges are seen. We note that

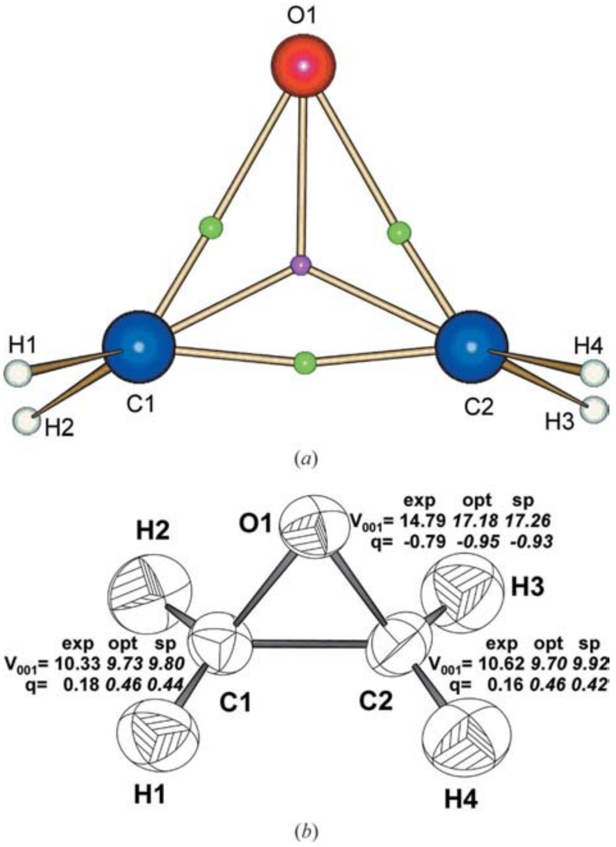


Figure 1
(*a*) *SCHAKAL* plot (Keller & Pierrard, 1999) of the molecular structure of ethylene oxide, also showing the bond and ring critical points. (*b*) *ORTEP* (Burnett & Johnson, 1996) representation of the molecular structure in the crystal at 100 K with atomic numbering scheme, displacement ellipsoids at a 50% probability level and atomic properties V_{001} (in Å^3) and q_{001} (in e). First column: experiment, second column: theory at optimized geometry (opt); third column: theory at experimental geometry (singlepoint, *sp*).

Table 2
Bond-topological properties of ethylene oxide.

For the bond and ring entries, the first line refers to experimental results, the second/third line refers to theoretical results from optimized geometry/single-point calculation at experimental geometry.

Bond	Distance (Å)	Path (Å)	ρ(b.c.p.) (e Å^{-3})	$\nabla^2\rho$(b.c.p.) (e Å^{-5})	ϵ
O1—C1	1.4334 (7)	1.4334	1.68 (2)	−2.8 (1)	0.54
	1.4277	1.4295	1.72	−9.0	0.69
	1.4334	1.4334	1.70	−9.1	0.71
O1—C2	1.4417 (6)	1.4420	1.80 (1)	−9.0 (1)	0.51
	1.4273	1.4291	1.72	−9.1	0.68
	1.4417	1.4440	1.67	−8.6	0.79
C1—C2	1.4568 (8)	1.4644	1.72 (1)	−7.6 (1)	0.58
	1.4629	1.4780	1.76	−14.5	0.28
	1.4568	1.4718	1.79	−15.2	0.25
C—H(av.)	1.10	1.10	1.79 (6)	−16.9 (1)	0.04
	1.08	1.08	1.98	−26.3	0.03
	1.10	1.10	1.92	−24.8	0.03
Ring CP			1.42	8.5	
			1.47	6.1	
			1.46	6.3	

Contact	O···C (Å)	O···H (Å)	ρ(b.c.p.) (e Å^{-3})	$\nabla^2\rho$(b.c.p.) (e Å^{-5})	O···H—C (°)
O1···H2—C1^{i}	3.4807 (7)	2.4939 (6)	0.042	0.74	148.79 (1)
O1···H4—C2^{ii}	3.5029 (7)	2.5271 (5)	0.033	0.58	147.34 (3)
O1···H1—C1^{iii}	3.5818 (7)	2.5914 (6)	0.037	0.58	149.48 (1)

Symmetry codes: (i) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z$; (iii) $-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z$.

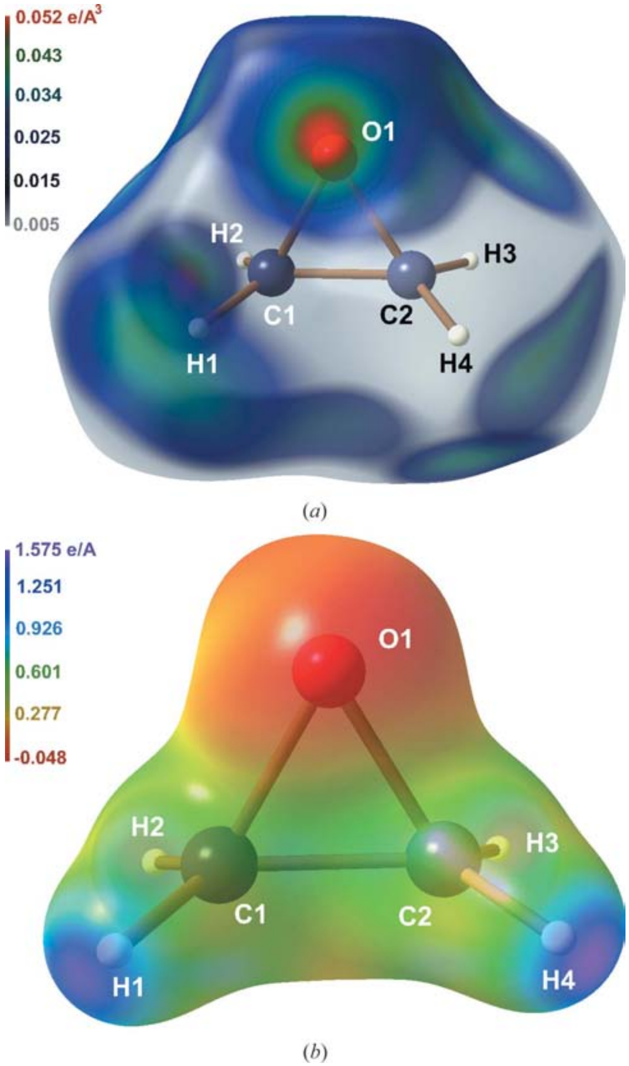
the above-discussed experimental bond-topological and atomic properties are in good agreement with corresponding results obtained from density-functional calculations [B3LYP/6-311++G(3df,3pd)] of the isolated molecule at experimental and optimized geometry (Frisch *et al.*, 1998).

There are three intermolecular C—H···O contacts with H···O distances below 2.6 Å, the shortest is H2···O1 = 2.49 Å. Bond-critical points were located on all three contacts with ρ(b.c.p.) values of 0.033–0.042 e Å^{-3}, which are indicative of rather weak interactions (Table 2).

Nevertheless, these contacts are visible as local density concentrations on the Hirshfeld surface (Fig. 2*a*; Spackman & Byrom, 1997). Moreover, the electrostatic potential mapped on the ED isosurface at 0.5 e Å^{-3} (Fig. 2*b*) shows that the strongest positive charges are around the three H atoms which contribute to the contacts, but not around H3 which is not involved in any close contacts. Although the C—H···O contacts are weak, it follows that they have a non-negligible influence on the charge distribution.

4. Conclusions

The general finding of this study is that despite the high strain in the three-membered ring of the title compound, most atomic and bond-topological properties do not differ from comparable fragments in unstrained molecules. As a special case the C—C bond can be considered which is significantly shorter than a C—C single bond, but has a ρ(b.c.p.) of normal C—C single bonds. The high strain of the molecule is expressed by the high ellipticities of the three bonds in this ring and the high electron density value at the ring critical point. It is not reflected well in the bond paths which have practically the same lengths as the internuclear vector for C—O. For C—C the bond path is less than 0.01 Å longer.



(*a*)

(*b*)

Figure 2
(*a*) Electron density mapped on the Hirshfeld surface (Spackman & Byrom, 1997) of ethylene oxide (legend in e Å^{-3}). The influence of the C—H···O contacts is visible in strongly coloured regions. (*b*) Electrostatic potential mapped on an electron-density isosurface at $\rho(\mathbf{r})$ = 0.5 Å^{-3} (legend in e Å^{-1}). Both illustrations are generated with *MolIso* (Hübschle & Luger, 2006).

Support of this work is gratefully accepted from the DFG within the special priority program 1178, grant Lu222/29-2.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1992). *International Tables for X-ray Crystallography*, Vol. C, ch. 9.5, pp. 685–706. Amsterdam: Kluwer Academic Publishers.

Bader, R. F. W. (1994). *Atoms in Molecules: A Quantum Theory*, 2nd ed. Oxford: Clarendon Press.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Frisch, M. J. *et al.* (1998). *GAUSSIAN*98, Revision A.7. Gaussian Inc., Pittsburgh PA.

Hansen, N. K. & Coppens, P. (1978). *Acta Cryst.* A**34**, 909–921.

Hirshfeld, F. L. (1976). *Acta Cryst.* A**32**, 239–244.

Hübschle, C. B. & Luger, P. (2006). *J. Appl. Cryst.* **39**, 901–904.

Jaradat, D. M. M., Mebs, S., Checinska, L. & Luger, P. (2007). *Carbohydr. Res.* **352**, 1480–1489.

Keller, E. & Pierrard, J.-S. (1999). *SCHAKAL*99. University of Freiburg, Germany.

Koritsánszky, T., Buschmann, J. & Luger, P. (1996). *J. Phys. Chem.* **100**, 10547–10553.
Luger, P. & Buschmann, J. (1983). *Angew. Chem. Int. Ed.* **22**, 537–542.
Luger, P. & Buschmann, J. (1984). *J. Am. Chem. Soc.* **106**, 7118–7121.
Luger, P., Zaki, C., Buschmann, J. & Rudert, R. (1986). *Angew. Chem. Int. Ed.* **25**, 276–277.
Madsen, A. Ø. (2006). *J. Appl. Cryst.* **39**, 757–758.
Scheins, S. (2002). Diploma thesis. Institute of Chemistry/Crystallography, FU Berlin, Germany.
Scheins, S., Messerschmidt, M., Dittrich, B., Morgenroth, W., Paulman, C. & Luger, P. (2007). *J. Phys. Chem.* **111**, 5499–5508.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spackman, M. A. & Byrom, P. G. (1997). *Chem. Phys. Lett.* **267**, 215.
Volkov, A., Abramov, Y. A. & Coppens, P. (2001). *Acta Cryst.* A**57**, 272–282.
Volkov, A., Macchi, P., Farrugia, L. J., Gatti, C., Mallinson, P. R., Richter, T. & Koritsanszky, T. (2006). *XD*2006. University at Buffalo, NY; University of Milano, Italy; University of Glasgow, UK; CNRISTM, Milano, Italy; Middle Tennessee State University, TN, USA.