

all about 120° [$118.2(1.2)$ – $122.8(1.2)^\circ$]. For (1) all the H atoms were successfully refined and a small degree of strain was found to result from the short N(10)–C(10a) bond. The bond angles H(1)–C(1)–C(10a) and H(9)–C(9)–C(9a) are less than 120° [$113(2)$ and $111(2)^\circ$ respectively]; the atoms H(1) and H(9) are forced inwards as the longer C–O(5) bond lengths cause the atoms H(4) and H(6) to be splayed outwards with H(4)–C(4)–C(4a) and H(6)–C(6)–C(5a) angles of $125(2)$ and $122(2)^\circ$. This is also reflected in the differences between the angles of $118.9(6)$ and $116.8(6)^\circ$ at O(5) and N(10).

The 7-methoxy substituent is twisted only slightly out of the [C₁₂NO] least-squares plane with deviations of O(7) and C(71) of $0.37(1)$ and $0.21(1)$ Å, respectively.

The only intramolecular contact of significance is between O(3) and H(N2a) of $2.33(6)$ Å. Only weak intermolecular interactions occur (Table 2).

References

- BROCKMANN, H. & MUXFELDT, H. (1958). *Chem. Ber.* **91**, 1242–1265.

- CANTRELL, J. S., WEBB, N. C. & MABIS, A. J. (1969). *Acta Cryst.* **B25**, 150–156.
 CHARALAMBOUS, J., KENSETT, M. J. & JENKINS, J. M. (1977). *J. Chem. Soc. Chem. Commun.* pp. 400–401.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 GILLEAN, J. A. III, PHELPS, D. W. & CORDES, A. W. (1973). *Acta Cryst.* **B29**, 2296–2298.
 HOSOYA, S. (1966). *Acta Cryst.* **20**, 429–432.
 IONESCU, M. & MANTSCH, H. (1967). *Adv. Heterocycl. Chem.* **8**, 83–113.
 JAIN, S. C. & SOBELL, H. M. (1972). *J. Mol. Biol.* **68**, 1–20.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 MCDOWELL, J. J. H. (1976). *Acta Cryst.* **B32**, 5–10.
 RIGANTI, V., LOCCHI, S., CURTI, R. & BOVIO, B. (1965). *J. Heterocycl. Chem.* **2**, 87–90, 176–180.
 SCHWETZ, B. A., NORRIS, J. M., SPARCHU, G. L., ROWE, V. K., GEHRING, P. J., EMERSON, J. L. & GERBIG, C. G. (1973). *Adv. Chem. Ser.* **120**, 55–69.
 SHELDRIK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SINGH, P. & MCKINNEY, J. D. (1978). *Acta Cryst.* **B34**, 2956–2957.
 SINGHABHANDHU, A., ROBINSON, P. D., FANY, J. H. & GEIGER, W. E. (1975). *Inorg. Chem.* **14**, 318–323.

Acta Cryst. (1982). **B38**, 291–294

A Neutron Diffraction Study of 1,1'-Ethylenebis(piperidine 1-oxide) Monoperchlorate*

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Abstract. C₁₂H₂₅N₂O₂⁺.ClO₄⁻ [PEtP(NO)₂.HClO₄], triclinic, *P*1̄, *a* = 6.281(1), *b* = 12.443(1), *c* = 10.490(1) Å, α = 102.48(1), β = 99.18(1), γ = 85.84(1)°, *Z* = 2, μ(measured) = 0.285 mm⁻¹ for λ =

1.210 Å. Final *R* = 0.060 for 2037 reflexions and 416 parameters. The intramolecular O···H···O bridge is 2.429(5) Å with an O···H···O angle of 175.1(6)°. The proton is, within experimental error, centrally located in the bridge, the two O···H distances being 1.225(7) and 1.206(7) Å. Thermal motion within the hydrogen-bond bridge indicates a single-minimum potential well. The geometry of the PEtP(NO)₂ skeleton is practically identical with that deduced from X-ray data.

* Hydrogen Bond Studies. CXLIII. Part CXLII: Küppers, Kvik & Olovsson (1981).

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Introduction. This is the fourth part of a series of diffraction studies of systems containing a PEtP-(NO)₂ skeleton. The previous paper reported an X-ray structure of PEtP(NO)₂.HClO₄ with a very short intramolecular O...H...O hydrogen bond [2.426 (3) Å] in the cation (Jaskólski, Gdaniec & Kosturkiewicz, 1981, hereafter JGK). The present neutron diffraction investigation of PEtP(NO)₂.HClO₄ has been undertaken in order to study the properties of this hydrogen bond.

Unit-cell parameters were redetermined by averaging the values obtained from least-squares fits of the setting angles of 15–20 high-angle reflexions measured on an

X-ray diffractometer for three different crystals. They are in reasonable agreement with those given by JGK.

Neutron diffraction data were collected for a single crystal with well-developed natural faces ({010}, {001}, {110}, {111}) and with dimensions 2.1 × 4.3 × 7.0 mm on a computer-controlled four-circle Hilger & Watts diffractometer at the Swedish R2 reactor at Studsvik using a beam with a mean wavelength of 1.210 Å ($\Delta\lambda/\lambda \sim 0.08$). A total of 2407 reflexions with $\sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$ were measured at 294 K. Two check reflexions monitored at regular intervals during the data collection indicated no systematic variation of intensity with time. The intensities were corrected for background using the profile analysis method of Lehmann & Larsen (1974) and for Lorentz and absorption effects. The minimum and maximum transmission factors were 0.34 and 0.66 respectively.

Table 1. Final fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters $B_{\text{iso}}^{\text{eq}}$ equivalent to anisotropic temperature factors (Willis & Pryor, 1975)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}^{\text{eq}}$ (Å ²)
H(O)	5737 (10)	1394 (5)	5614 (6)	3.9 (2)
H(121)	8300 (10)	3532 (6)	8206 (6)	4.5 (2)
H(122)	8519 (10)	2114 (5)	7396 (6)	4.4 (2)
H(131)	5957 (14)	1639 (7)	8668 (8)	5.8 (2)
H(132)	8113 (14)	2339 (6)	9743 (7)	5.8 (2)
H(141)	5889 (15)	4044 (7)	10061 (8)	6.8 (3)
H(142)	4429 (17)	3010 (9)	10402 (9)	7.9 (3)
H(151)	2314 (12)	2729 (8)	8162 (9)	6.8 (3)
H(152)	2141 (13)	4161 (7)	8937 (9)	7.2 (3)
H(161)	4933 (13)	4583 (6)	7778 (7)	5.6 (2)
H(162)	2790 (13)	3915 (7)	6611 (9)	6.5 (2)
H(11)	5010 (14)	3490 (6)	5042 (7)	5.9 (2)
H(12)	7086 (15)	4181 (6)	6204 (8)	6.1 (2)
H(21)	9611 (13)	2498 (7)	5786 (7)	5.6 (2)
H(22)	8793 (15)	3162 (6)	4461 (8)	6.1 (2)
H(221)	6296 (14)	2328 (6)	2638 (7)	6.0 (2)
H(222)	4412 (12)	2057 (6)	3614 (7)	5.3 (2)
H(231)	4041 (17)	803 (8)	1424 (9)	8.1 (3)
H(232)	4788 (13)	69 (7)	2711 (8)	5.9 (2)
H(241)	7830 (17)	672 (7)	992 (8)	7.2 (3)
H(242)	7000 (17)	-657 (7)	935 (8)	7.3 (3)
H(251)	8689 (13)	-611 (6)	3218 (8)	5.8 (2)
H(252)	10633 (16)	-314 (7)	2310 (9)	6.9 (3)
H(261)	10796 (13)	962 (7)	4492 (8)	5.9 (2)
H(262)	10140 (12)	1670 (7)	3158 (8)	5.6 (2)
O(1)	4517 (6)	1987 (3)	6291 (3)	3.41 (9)
O(2)	7037 (6)	876 (3)	4968 (3)	3.44 (9)
N(1)	5642 (3)	2951 (2)	6827 (2)	2.90 (5)
C(12)	7468 (5)	2756 (3)	7884 (3)	2.87 (8)
C(13)	6663 (6)	2427 (3)	9016 (3)	3.8 (1)
C(14)	5053 (6)	3273 (4)	9616 (4)	4.8 (1)
C(15)	3231 (6)	3479 (3)	8551 (4)	4.8 (1)
C(16)	4053 (6)	3809 (3)	7426 (4)	4.1 (1)
C(1)	6449 (6)	3357 (3)	5750 (3)	3.7 (1)
C(2)	8224 (6)	2678 (3)	5084 (4)	3.6 (1)
N(2)	7624 (3)	1585 (2)	4219 (2)	2.91 (6)
C(22)	5812 (6)	1718 (3)	3132 (3)	3.8 (1)
C(23)	5341 (7)	638 (3)	2176 (4)	4.5 (1)
C(24)	7323 (7)	130 (4)	1586 (4)	4.9 (1)
C(25)	9141 (7)	-11 (3)	2693 (4)	4.3 (1)
C(26)	9618 (6)	1074 (3)	3650 (4)	3.8 (1)
Cl	820 (4)	3755 (2)	2316 (2)	3.50 (7)
O(3)	1152 (9)	4532 (4)	1583 (6)	6.6 (2)
O(4)	1269 (9)	2669 (3)	1635 (5)	6.1 (2)
O(5)	2134 (11)	3927 (5)	3563 (6)	8.8 (2)
O(6)	-1375 (8)	3828 (5)	2490 (6)	6.9 (2)

The full-matrix least-squares refinement of the structure started from the X-ray parameters given by JGK and was based on 2037 reflexions with $I \geq 0.5\sigma(I)$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = \sigma^{-2}(F_o) + 0.03F_o^2$ and $\sigma(F_o)$ derived from counting statistics. The parameters varied in the least-squares calculations comprised positional and anisotropic thermal parameters of all atoms, the scale factor and an isotropic extinction coefficient. The isotropic extinction model used was that described by Becker & Coppens (1974*a,b*, 1975) as type I (mosaic-spread dominated) with Lorentzian mosaic-spread distribution. The refined extinction parameter is $1.45 (7) \times 10^4$ and corresponds to a r.m.s. spread of 4". The refinement indicated that the extinction was not severe since none of the reflexions suffered more than 50% intensity loss from it and only 3.9% of the data were affected by more than 15%. Coherent scattering amplitudes were taken from Koester (1977). The refinement converged at $R = 0.060$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.061$. The number of reflexions per parameter in the final refinement was 4.9. Final positional and isotropic thermal ($B_{\text{iso}}^{\text{eq}}$) parameters of all atoms are given in Table 1.*

All calculations were carried out on NORD-100 and IBM 370 computers using programs described by Lundgren (1979).

Discussion. Bond distances and angles in the hydrogen-bonded PEtP(NO)₂.H⁺ skeleton are shown in Fig. 1, together with the X-ray values found by JGK (marked with an asterisk). There is close agreement between these two parameter sets in the PEtP moiety of the cation. Most of the differences are less than 1σ and only a few approach 2σ . The striking features of the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36206 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cation geometry demonstrating the strain within the skeleton reported by JGK [deviation of the N(2)—C(2)—C(1) and N(1)—C(1)—C(2) angles from the tetrahedral value by more than 7°] are further confirmed by this neutron study. The N—O distances as found in this study and by JGK are 1.401 (4) and 1.411 (3) Å, respectively, for N(1)—O(1) and 1.404 (4) and 1.412 (3) Å for N(2)—O(2). Although the differences are within the experimental errors, the fact that both N—O bonds are longer in the X-ray case by almost the same amount (0.008, 0.010 Å) may be taken as an indication that these differences are not only of random character. It is, however, difficult to give a satisfactory explanation for this discrepancy. The average piperidyl C—C distance is 1.513 Å while the average piperidyl N—C bond length (quaternary nitrogen) is 1.509 Å. The C—H bond lengths (Table 2) range from 1.071 (9) to 1.108 (8) Å with a mean of 1.094 Å. The H—C—H and C—C—H angles are between 105.8 (5) and 113.9 (5)°, the mean value being 109.6°, whereas the N—C—H angles cover appreciably lower values from 105.2 (5) to 107.0 (5)° with a mean of 106.1°.

The O...O distance of the intramolecular hydrogen bond is 2.429 (5) Å and agrees well with that,

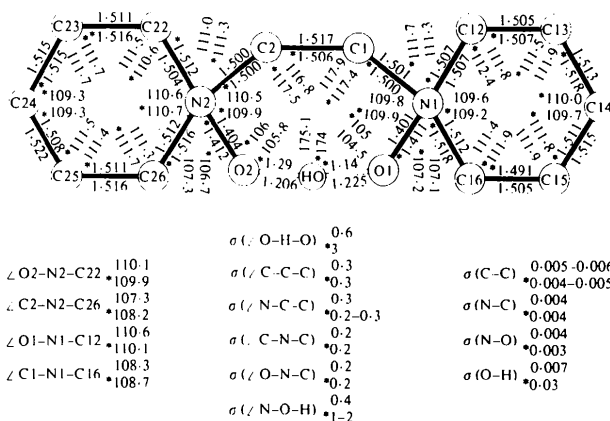


Fig. 1. Bond distances (Å) and angles (°) in the PEtP(NO)₂.H⁺ cation (carbon H atoms are not shown) as found in this neutron study and in the X-ray study (JGK, indicated by asterisks).

Table 2. C—H bond distances (Å)

C(12)—H(121)	1.093 (7)	C(22)—H(221)	1.091 (8)
C(12)—H(122)	1.091 (7)	C(22)—H(222)	1.097 (8)
C(13)—H(131)	1.071 (9)	C(23)—H(231)	1.083 (11)
C(13)—H(132)	1.106 (9)	C(23)—H(232)	1.098 (9)
C(14)—H(141)	1.102 (10)	C(24)—H(241)	1.105 (10)
C(14)—H(142)	1.086 (11)	C(24)—H(242)	1.077 (10)
C(15)—H(151)	1.099 (10)	C(25)—H(251)	1.096 (9)
C(15)—H(152)	1.099 (9)	C(25)—H(252)	1.089 (10)
C(16)—H(161)	1.108 (8)	C(26)—H(261)	1.085 (9)
C(16)—H(162)	1.094 (9)	C(26)—H(262)	1.085 (9)
C(1)—H(11)	1.102 (9)	C(2)—H(21)	1.091 (9)
C(1)—H(12)	1.107 (8)	C(2)—H(22)	1.092 (9)

2.426 (3) Å, found by JGK. Also the values for the O(1)...H(O)...O(2) angle are in close agreement: 175.1 (6) and 174 (3)° respectively. The two chemically equivalent but crystallographically non-equivalent O...H distances are 1.225 (7) and 1.206 (7) Å [X-ray values: 1.14 (3) and 1.29 (3) Å respectively]. With the present data the assumption that the proton occupies a central position in the hydrogen bridge cannot be rejected since a statistical test (Cruickshank & Robertson, 1953) indicates more than 5% probability for the difference between these two bonds [0.019 (10) Å] being random. This, and the close similarity of the molecular geometry in the two chemically equivalent moieties of the cation, suggests that the potential well of the proton is approximately symmetrical. A thermal-ellipsoid stereoscopic drawing of the cation including all the H atoms is shown in Fig. 2. It can be seen that the piperidyl rings of the cation protect the hydrogen-bond bridge from exposure to short intermolecular contacts. Fig. 2 and Table 3 also

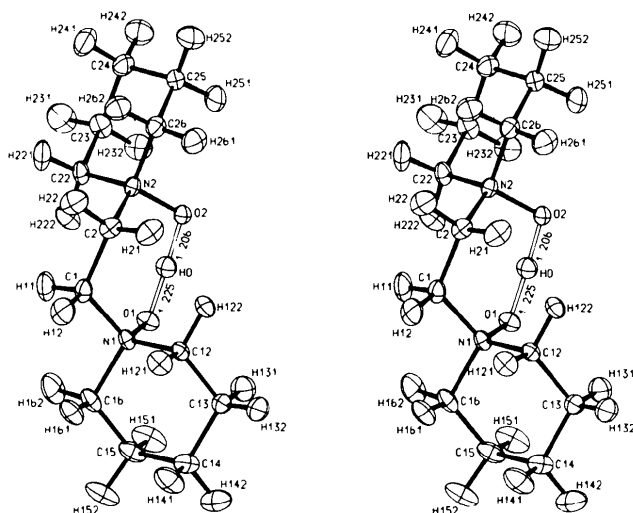


Fig. 2. ORTEP (Johnson, 1976) thermal-ellipsoid stereodrawing of the cation. The thermal ellipsoids are scaled to enclose 20% probability.

Table 3. Thermal motion of the atoms in the O...H...O bridge

	R.m.s. displacement along principal axis (Å)	Angle between principal axis and O(1)...O(2) vector (°)	R.m.s. displacement in O(1)...O(2) direction (Å)
H(O)	0.203 (8)	105 (16)	
	0.226 (9)	17 (17)	0.225 (9)
	0.240 (8)	83 (23)	
O(1)	0.157 (6)	107 (5)	
	0.206 (5)	161 (5)	0.203 (5)
	0.250 (4)	97 (5)	
O(2)	0.178 (5)	103 (9)	
	0.204 (5)	14 (8)	0.203 (5)
	0.240 (5)	85 (6)	

show that the directions of the largest thermal displacements of the three hydrogen-bridge atoms [O(1), H(O), O(2)] are roughly normal to the O(1)···O(2) hydrogen-bond line. The thermal ellipsoid of each of these atoms has one of its principal axes roughly along the O(1)···O(2) vector and the other two approximately perpendicular to it. An analysis similar to that by Ellison & Levy (1965) for potassium hydrogen chloromaleate has been carried out to study whether H(O) effectively vibrates in a single- or double-minimum potential well: subtracting the mean-square component of displacement of O(1) and O(2) along the O(1)···O(2) vector [both equal to 0.041 (2) Å²] from the corresponding value for H(O) yields 0.009 (4) Å² as the mean-square amplitude of stretching of the O···H link in the hydrogen bridge. From spectroscopic data (Jaskólski, Kosturkiewicz, Mickiewicz-Wichłacz & Wiewiórowski, 1979) it is suggested that the mean-square amplitude for the O···H stretching cannot be significantly smaller than this value. The conclusion is accordingly that the potential is effectively of the single-minimum type. Additional investigations are planned involving a low-temperature neutron diffraction study and a more accurate spectroscopic investigation for comparative studies.

The geometry of the perchlorate anion is given in Table 4. The values in this table as well as the thermal

parameters of the ClO₄⁻ atoms both agree with the corresponding data reported by JGK.

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References

- BECKER, P. & COPPENS, P. (1974*a*). *Acta Cryst.* **A30**, 129–147.
 BECKER, P. & COPPENS, P. (1974*b*). *Acta Cryst.* **A30**, 148–153.
 BECKER, P. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.
 CRUICKSHANK, D. W. J. & ROBERTSON, A. P. (1953). *Acta Cryst.* **6**, 698–705.
 ELLISON, R. D. & LEVY, H. A. (1965). *Acta Cryst.* **19**, 260–268.
 JASKÓLSKI, M., GDANIEC, M. & KOSTURKIEWICZ, Z. (1981). *Pol. J. Chem.* Submitted for publication.
 JASKÓLSKI, M., KOSTURKIEWICZ, Z., MICKIEWICZ-WIHLACZ, D. & WIEWIÓROWSKI, M. (1979). *J. Mol. Struct.* **52**, 77–94.
 JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
 KOESTER, L. (1977). *Springer Tracts Mod. Phys.* **80**, 1–55.
 KÜPPERS, H., KVICK, Å. & OLOVSSON, I. (1981). *Acta Cryst.* **B37**, 1203–1207.
 LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
 LUNDGREN, J.-O. (1979). *Crystallographic Computer Programs*. Report UUIC-B13-4-04. Institute of Chemistry, Univ. of Uppsala.
 WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 101–102. Cambridge Univ. Press.

Table 4. *Geometry of the ClO₄⁻ anion*

Cl—O(3)	1.403 (6) Å	Cl—O(5)	1.414 (7) Å
Cl—O(4)	1.417 (5)	Cl—O(6)	1.414 (6)
O(3)—Cl—O(4)	111.1 (3)°	O(4)—Cl—O(5)	108.0 (4)°
O(3)—Cl—O(5)	112.1 (4)	O(4)—Cl—O(6)	107.5 (4)
O(3)—Cl—O(6)	108.6 (4)	O(5)—Cl—O(6)	109.5 (4)