Crystal Structure of Trimethyl-[4-(2-oxopyrrolidin-1-yl)but-2-ynyl]ammonium Iodide

By **Roy W. Baker** * and **Peter J. Pauling**, William Ramsay, Ralph Forster, and Christopher Ingold Laboratories, University College, Gower Street, London WC1H 0A

The structure of the title compound has been determined by single-crystal *X*-ray diffraction. Crystals are triclinic with $Z = 2$ in a unit cell of dimensions $a = 9{\cdot}382(4)$, $b = 7{\cdot}502(3)$, $c = 11{\cdot}166(4)$ Å, $\alpha = 111{\cdot}13(5)$, $\beta = 69{\cdot}89(5)$, $\gamma = 93{\cdot}23(5)^\circ$, space group $P\bar{1}$. The structure was solved by Patterson and Fourier methods and refined by least-squares to R 0·051 for 2501 observed three-dimensional diffractometer data. The amide group N(1), C(5), O(1), C(6) is planar and the orientation of the trimethylammonium group is symmetrical with respect to C(3)–C(4) such that τ [C(3)–C(4)–N(2)–C(10)] is almost 180°.

Oxotremorine [1-(2-oxopyrrolidin-1-yl)-4-(pyrrolidin-1-yl)but-2-yne] is a cholinergic agent which is used experimentally as a convulsant in the study of Parkinsonism.[1] The title compound is related to oxotremorine in that it is a tremorgenic agent and differs in chemical structure only by having a trimethylammonium group in place of the pyrrolidin-1-yl group on C(4) (Figure 1). We have determined the crystal structure of the trimethylammonium iodide compound as part of a research programme on structure–activity correlations of compounds affecting the nervous systems, and present here the results of the structure analysis.

EXPERIMENTAL

Crystals of the iodide are badly formed colourless plates which show biaxial interference figures.

Crystal Data.—$C_{11}H_{19}IN_2O$, $M = 322{\cdot}2$. Triclinic, $a = 9{\cdot}382(4)$, $b = 7{\cdot}502(3)$, $c = 11{\cdot}166(4)$ Å, $\alpha = 111{\cdot}13(5)$, $\beta = 69{\cdot}89(5)$, $\gamma = 93{\cdot}23(5)^\circ$, $U = 686$ Å^3, $D_m = 1{\cdot}58(1)$ (by flotation), $Z = 2$, $D_c = 1{\cdot}56$. Space group $P1$ or $P\bar{1}$, shown to be the latter by subsequent successful refinement. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 24{\cdot}4$ cm^{-1}.

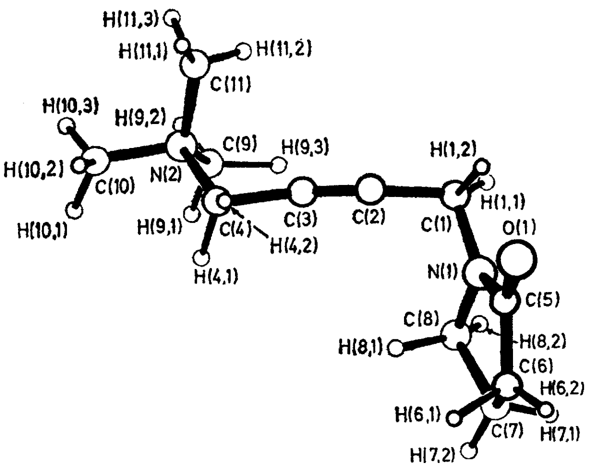

FIGURE 1 Atomic numbering and perspective view of the molecule

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[1] The Merck Index, 1968, 8th edn.

TABLE 1

Fractional co-ordinates (× 10^4) and thermal motion parameters * (× 10^4) for non-hydrogen atoms, derived from the least-squares refinement, with estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I(1)	1834(1)	3135(1)	1819(1)	442(4)	542(2)	503(5)	40(2)	−133(2)	209(2)
C(1)	7646(12)	2774(13)	4694(10)	911(70)	562(54)	469(48)	−37(48)	−341(50)	217(43)
C(2)	7107(11)	2600(13)	3562(9)	629(55)	612(54)	440(48)	−71(42)	−198(41)	255(41)
C(3)	6755(10)	2294(12)	2589(9)	528(47)	525(49)	483(48)	2(39)	−183(39)	190(40)
C(4)	6259(9)	1750(12)	1395(8)	532(47)	496(44)	454(43)	−116(36)	−206(37)	247(36)
N(1)	7784(8)	0902(10)	4770(7)	582(43)	560(42)	362(34)	57(33)	−113(30)	181(31)
C(5)	6703(10)	0284(13)	5671(8)	535(47)	492(52)	362(43)	40(40)	−154(37)	154(38)
C(6)	7049(12)	−1829(14)	5253(9)	762(63)	616(57)	483(53)	82(48)	−122(46)	250(45)
C(7)	8631(12)	−2272(15)	4176(11)	653(63)	676(64)	667(63)	200(50)	−209(50)	129(50)
C(8)	8803(11)	−0679(14)	3612(10)	559(55)	673(62)	517(53)	65(45)	−22(43)	140(37)
O(1)	5623(8)	1309(10)	6637(7)	770(47)	718(44)	474(34)	160(36)	39(33)	83(33)
N(2)	6946(7)	3020(9)	0561(6)	430(35)	459(35)	401(34)	−2(28)	−178(28)	176(28)
C(9)	8661(9)	2735(14)	0046(9)	371(43)	779(64)	551(53)	−59(40)	−130(37)	276(47)
C(10)	6426(10)	2360(13)	−0653(9)	575(51)	668(57)	440(43)	−19(42)	−272(41)	212(41)
C(11)	6370(12)	5073(13)	1412(9)	919(74)	451(49)	503(53)	146(47)	−311(50)	45(40)

* The Debye–Waller factor is defined as $T = \exp[-2\pi^2 \sum_i \sum_j a_i^* a_j^* h_i h_j U_{ij}]$ with U_{ij} in Å².

Intensity Measurement.—Three dimensional X-ray diffraction data from a small single crystal fragment (*ca.* 0·20 × 0·27 × 0·34 mm) were collected on a computer-controlled [2] four-circle diffractometer by use of Mo-K_α radiation with graphite monochromator (002). A coupled θ—2θ step scan with $\Delta 2\theta$ 0·04°, a counting time of 5 s per step and a peakwidth of 1·6° were used. In the range $2\theta = 5$—55°, 3573 observations covering one half of reciprocal space were collected. This number reduced to 3180 symmetry-independent reflections of which 2501 were defined as observed having $I \geqslant 3\sigma(I)$. The data were corrected for Lorentz and polarisation effects but not for absorption or extinction.

Structure Solution and Refinement.—The space group was assumed to be $P\bar{1}$ and the position of the iodine atom in the asymmetric unit was determined from an unsharpened Patterson synthesis [3] from data collected in the range $2\theta = 5$—45° (1605 observed intensities). A Fourier synthesis [3] with the 1605 observed data phased by the iodine atom produced a satisfactory trial structure. Three cycles of full-matrix least-squares refinement [4] of positional and isotropic thermal parameters and an overall scale-factor for the non-hydrogen atoms gave R 0·082 for the 1605 data.

TABLE 2

Fractional co-ordinates (× 10^3) for hydrogen atoms * derived from difference-Fourier synthesis

Atom	x	y	z	Atom	x	y	z
H(1,1)	876	325	465	H(9,1)	901	142	−058
H(1,2)	687	352	567	H(9,2)	908	365	−049
H(4,1)	661	026	073	H(9,3)	915	293	095
H(4,2)	533	174	200	H(10,1)	540	221	−034
H(6,1)	621	−285	471	H(10,2)	686	106	−137
H(6,2)	693	−218	592	H(10,3)	693	315	−127
H(7,1)	945	−219	457	H(11,1)	524	546	176
H(7,2)	886	−356	342	H(11,2)	680	555	199
H(8,1)	835	−122	276	H(11,3)	699	618	084
H(8,2)	990	−032	343				

* Numbered according to the atom to which they are bonded. A thermal motion parameter $U = 0{\cdot}045$ Å² is assumed for all hydrogen atoms.

TABLE 3

Interatomic distances (Å) and bond angles (°), with estimated standard deviations in parentheses

(*a*) Distances

C(1)–C(2)	1·48(1)	C(4)–H(4,2)	0·90(15)
C(1)–N(1)	1·45(1)	C(6)–H(6,1)	1·22(15)
C(2)–C(3)	1·18(1)	C(6)–H(6,2)	0·84(15)
C(3)–C(4)	1·47(1)	C(7)–H(7,1)	1·00(15)
C(4)–N(2)	1·53(1)	C(7)–H(7,2)	1·00(15)
N(1)–C(5)	1·36(1)	C(8)–H(8,1)	1·11(15)
N(1)–C(8)	1·47(1)	C(8)–H(8,2)	1·02(15)
C(5)–C(6)	1·50(1)	C(9)–H(9,1)	0·97(15)
C(5)–O(1)	1·23(1)	C(9)–H(9,2)	1·04(15)
C(6)–C(7)	1·52(2)	C(9)–H(9,3)	1·21(15)
C(7)–C(8)	1·52(2)	C(10)–H(10,1)	0·92(15)
N(2)–C(9)	1·51(1)	C(10)–H(10,2)	1·01(51)
N(2)–C(10)	1·51(1)	C(10)–H(10,3)	1·04(15)
N(2)–C(11)	1·50(1)	C(11)–H(11,1)	1·02(15)
C(1)–H(1,1)	1·08(15)	C(11)–H(11,2)	0·84(15)
C(1)–H(1,2)	1·04(15)	C(11)–H(11,3)	1·23(15)
C(4)–H(4,1)	1·09(15)		

(*b*) Angles

C(2)–C(1)–N(1)	110(1)	C(9)–N(2)–C(10)	109(1)
C(1)–C(2)–C(3)	174(1)	C(9)–N(2)–C(11)	112(1)
C(2)–C(3)–C(4)	175(1)	C(10)–N(2)–C(11)	109(1)
C(3)–C(4)–N(2)	110(1)	C(2)–C(1)–H(1,1)	119(8)
C(1)–N(1)–C(5)	123(1)	C(2)–C(1)–H(1,2)	115(8)
C(1)–N(1)–C(8)	121(1)	N(1)–C(1)–H(1,1)	101(8)
C(5)–N(1)–C(8)	113(1)	N(1)–C(1)–H(1,2)	101(8)
N(1)–C(5)–C(6)	108(1)	H(1,1)–C(1)–H(1,2)	109(12)
N(1)–C(5)–O(1)	125(1)	C(3)–C(4)–H(4,1)	112(8)
C(6)–C(5)–O(1)	127(1)	C(3)–C(4)–H(4,2)	85(8)
C(5)–C(6)–C(7)	105(1)	N(2)–C(4)–H(4,1)	109(8)
C(6)–C(7)–C(8)	104(1)	N(2)–C(4)–H(4,2)	134(8)
C(7)–C(8)–N(1)	103(1)	H(4,1)–C(4)–H(4,2)	106(12)
C(7)–C(6)–H(6,1)	106(8)	N(2)–C(9)–H(9,1)	111(8)
C(7)–C(6)–H(6,2)	116(8)	N(2)–C(9)–H(9,2)	107(8)
H(6,1)–C(6)–H(6,2)	102(12)	N(2)–C(9)–H(9,3)	113(8)
C(6)–C(7)–H(7,1)	113(8)	H(9,1)–C(9)–H(9,2)	108(12)
C(6)–C(7)–H(7,2)	117(8)	H(9,1)–C(9)–H(9,3)	104(12)
C(8)–C(7)–H(7,1)	107(8)	H(9,2)–C(9)–H(9,3)	114(12)
C(8)–C(7)–H(7,2)	111(8)	N(2)–C(10)–H(10,1)	107(12)
H(7,1)–C(7)–H(7,2)	104(12)	N(2)–C(10)–H(10,2)	117(12)
C(7)–C(8)–H(8,1)	105(8)	N(2)–C(10)–H(10,3)	109(12)
C(7)–C(8)–H(8,2)	108(8)	H(10,1)–C(10)–H(10,2)	103(12)
N(1)–C(8)–H(8,1)	111(8)	H(10,1)–C(10)–H(10,3)	125(12)
N(1)–C(8)–H(8,2)	109(8)	H(10,2)–C(10)–H(10,3)	97(12)
H(8,1)–C(8)–H(8,2)	120(12)	N(2)–C(11)–H(11,1)	120(8)
C(4)–N(2)–C(9)	110(1)	N(2)–C(11)–H(11,2)	111(8)
C(4)–N(2)–C(10)	107(1)	N(2)–C(11)–H(11,3)	113(8)
C(4)–N(2)–C(11)	110(1)	H(11,1)–C(11)–H(11,2)	115(12)
C(5)–C(6)–H(6,1)	115(8)	H(11,1)–C(11)–H(11,3)	105(12)
C(5)–C(6)–H(6,2)	114(8)	H(12,2)–C(11)–H(11,3)	89(12)

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[2] W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, U.S. At. Energy Commission, Report ORNL 143, 1968.

[3] J. Dollimore, A Fourier Program for LUNA, University of London Institute of Computer Science, Circular No. 1.2.

[4] G. Shearing, A Crystallographic SFLS Program in AA, University of Manchester, 1965.

Conversion to anisotropic thermal parameters and subsequent refinement over 2501 data led to R 0·057. At this stage a difference-electron density synthesis revealed all hydrogen atom positions. Hydrogen atom contribution to the calculated structure factors was included and the non-hydrogen atoms refined until all parameter shifts were $\leqslant 0{\cdot}10\sigma$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$ for all reflection data. Atomic scattering factors for neutral carbon, nitrogen, and oxygen and for the iodide ion were taken from ref. 5 and for hydrogen from ref. 6. The final R was 0·051. Positional and thermal parameters derived from the refinement are listed in Table 1, hydrogen atom positions derived from the difference synthesis in Table 2, and bond distances and angles[7] in Table 3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20699 (7 pp., 1 microfiche).*

All computational work was carried out on the University of London ATLAS computer and the University College IBM 360 computer.

DISCUSSION

Description of the Molecular Structure.—The atomic numbering scheme used in this analysis and configuration of the molecule as observed in the crystal is shown in Figure 1. The trimethylammonium group is symmetrically arranged with respect to the bond C(3)–C(4) such that τ[C(3)–C(4)–N(2)–C(10)] is almost 180° (Table 4). The bond lengths observed for the butyne group are not significantly different from those found in dimethylacetylene[8] or other compounds containing CH_3–C≡C– entities.[9-11] The bond angles about C(2) and C(3) (174, 175°) appear to differ from the expected 180° by $>3\sigma$. Whether this difference is really significant is open to speculation. Most intermolecular contacts, neglecting hydrogen atoms, are $>3{\cdot}6$ Å. The three contacts $<3{\cdot}6$ Å involve O(1) and are: O(1) · · · C(3) (at $1 - x, -y, 1 - z$) 3·57, O(1) · · · C(10) (at $x, y, 1 + z$) 3·18, and O(1) · · · C(11) (at $1 - x, 1 - y, 1 - z$) 3·02 Å. Figure 2 shows the molecular packing viewed normal to (001). The amide group O(1), N(1), C(5), C(6) is planar (Table 5) with C(7) and C(8) displaced from it by 0·26 and −0·18 Å. The non-planarity of the five-membered ring has also been found in two other 2-oxopyrrolidine structures[12] and their geometries are not significantly different from that observed in the present structure. The angle between the mean planes through C(10), N(2), C(4), and C(3), and N(1), O(1), C(5), and C(6) is 75° and the angle τ[N(2)–C(4)–C(1)–N(1)] is −143°.

TABLE 4

Torsion angles (deg.) for non-hydrogen atoms

C(1)–C(2)–C(3)–C(4)	58	C(3)–C(4)–N(2)–C(10)	179
C(1)–N(1)–C(5)–C(6)	167	C(3)–C(4)–N(2)–C(11)	−63
C(1)–N(1)–C(5)–O(1)	−11	N(1)–C(5)–C(6)–C(7)	11
C(1)–N(1)–C(8)–C(7)	177	N(1)–C(8)–C(7)–C(6)	27
C(2)–C(1)–N(1)–C(5)	−99	C(5)–N(1)–C(8)–C(7)	−22
C(2)–C(1)–N(1)–C(8)	60	C(5)–C(6)–C(7)–C(8)	−24
C(2)–C(3)–C(4)–N(2)	−169	C(6)–C(5)–N(1)–C(8)	7
C(3)–C(2)–C(1)–N(1)	−35	C(7)–C(6)–C(5)–O(1)	−170
C(3)–C(4)–N(2)–C(9)	61	C(8)–N(1)–C(5)–O(1)	−172

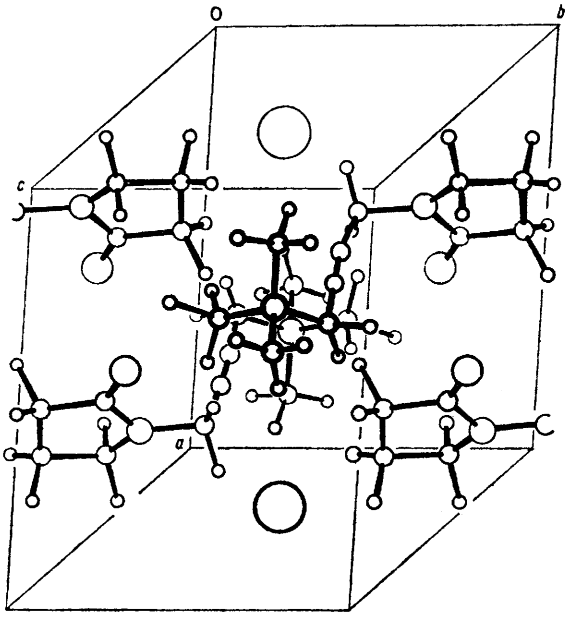

FIGURE 2 Unit-cell contents viewed normal to (001)

TABLE 5

Equations of best mean planes in the form $lX + mY + nZ = P$ where X, Y, Z refer to an orthonormalised co-ordinate system with X parallel to the crystallographic a axis, Y in the plane ab and perpendicular to X, and Z perpendicular to the plane ab and completing a right-handed set of axes X,Y,Z. Deviations (Å) of atoms from the plane are given in square brackets

Plane (1):

C(10), N(2), C(4), C(3) $0{\cdot}687X - 0{\cdot}490Y - 0{\cdot}537Z = 6{\cdot}679$

[C(10) 0·01, N(2) −0·01, C(4) −0·01, C(3) 0·01]

Plane (2):

N(1), O(1), C(5), C(6) $0{\cdot}810X - 0{\cdot}017Y + 0{\cdot}586Z = 10{\cdot}301$

[N(1) 0·00, O(1) 0·00, C(5) 0·01, C(6) 0·00, C(7) 0·26, C(8) −0·18]

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[7] J. Dollimore, A Distance Angle Program for LUNA, University of London Institute of Computer Science, Circular No. 4.

[8] E. Pignatoro and B. Post, *Acta Cryst.*, 1955, **8**, 672.

[9] R. C. Himes and P. M. Harris, Technical Report No. 3 RF, Project 355, Ohio State University.

[10] G. A. Jeffery and J. S. Rollett, *Proc. Roy. Soc.*, 1953, *A*, **86**, 213.

[11] H. Irngartinger, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1970, 497.

[12] J. A. Molin-Case, E. Fleischer, and D. W. Urry, *J. Amer. Chem. Soc.*, 1970, **92**, 4728.