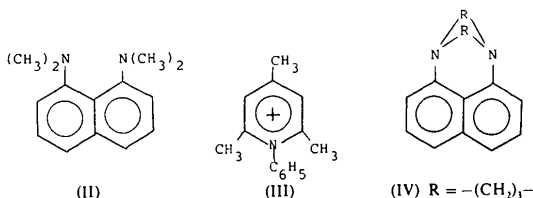


(dimethylamino)naphthalene (II), for example, *peri* interactions have forced one CH₃ of each (CH₃)₂N group out of the naphthalene plane, resulting in angle sums at both nitrogens of 347°; the average C(naphthalene)—N distance is 1.397 Å and the amount of π character in these bonds has been estimated at 20% (Einspahr, Robert, Marsh & Roberts, 1973). In the case of the tertiary nitrogen atom N(1), the angle sum of 318.4° clearly indicates a pyramidal geometry, and the arrangement of C(7) and C(8), respectively, above and below the benzene plane, suggests that the usual C(sp²)—N(amine) π -type conjugation must be minimal for C(2)—N(1). This possibility is supported by the 1.452 Å distance, which undoubtedly is close to that of a single C(sp²)—N(sp³) bond. Other C—N distances which provide points of reference are the C(sp³)—N(sp³) of 1.472 Å in methylamine (Sutton, 1965), the presumably pure single bond C(sp²)—N(sp²) of 1.470 Å in (III) (Camerman, Jensen & Balaban, 1969; Camerman, 1970), and the 1.425 Å in (IV) (Adler, Goode, King, Mellor & Miller, 1976), which might be classified as C(sp²)—N(sp²) based on the average angle sum of 356° at nitrogen. The difference between the C(sp²)—N(sp²) lengths in (III) and (IV) is presumably due to the different kinds of nitrogen atoms (\ddot{N} vs N⁺).



The intermolecular packing arrangement is limited to van der Waals contacts, with one exception. There is a weak N(4)—H(4)···N(1) interaction (2.08 Å) between

the N acceptor at x, y, z and the H donor at $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$

This work was supported by the National Institutes of Health (R01-AM17458). The crystallographic calculations were supported through the facilities of the Computer Science Center, University of Maryland.

References

- ADLER, R. W., GOODE, N. C., KING, T. J., MELLOR, J. M. & MILLER, B. W. (1976). *Chem. Commun.* pp. 173–174.
 CAMERMAN, A. (1970). *Can. J. Chem.* **48**, 179–181.
 CAMERMAN, A., JENSEN, L. H. & BALABAN, A. T. (1969). *Acta Cryst.* **B25**, 2623–2630.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 CUNNINGHAM, H. C. (1969). PhD Dissertation, Univ. of Pennsylvania; *Diss. Abstr. Int. B*, **30**, 2602.
 CUNNINGHAM, H. C. & DAY, A. R. (1973). *J. Org. Chem.* **38**, 1225–1227.
 EINSPAHR, H., ROBERT, J. B., MARSH, R. E. & ROBERTS, J. D. (1973). *Acta Cryst.* **B29**, 1611–1617.
 HUGHES, E. W. (1941). *J. Am. Chem. Soc.* **63**, 1737–1752.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 LARSON, A. C. (1970). *Crystallographic Computing*, edited by F. R. AHMED, S. R. HALL & C. P. HUBER, p. 291. Copenhagen: Munksgaard.
 STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions*. Suppl. 1956–1965. London: The Chemical Society.

Acta Cryst. (1979). **B35**, 1724–1727

Structure of Adenosine 5'-Methylphosphonate Hemihydrate

BY CHARLES L. BARNES AND STUART W. HAWKINSON

Department of Biochemistry, University of Tennessee, Knoxville, Tennessee 37916, USA

(Received 8 November 1978; accepted 4 April 1979)

Abstract. C₁₁H₁₆N₅O₆P·½H₂O, *P*1, $a = 10.510$ (2), $b = 9.419$ (2), $c = 7.803$ (2) Å, $\alpha = 76.77$ (1), $\beta = 97.24$ (2), $\gamma = 95.99$ (1)°, $Z = 2$, $D_c = 1.582$, $D_o = 1.576$ Mg m⁻³, $V = 743.7$ Å³, $FW = 354.3$, $\lambda(\text{Mo } K\alpha_1) = 0.70926$ Å, $T = 299 \pm 1$ K, $F(000) = 370$. The intensity data were collected on an automated diffractometer, and the structure was solved from a

0567-7408/79/071724-04\$01.00

sharpened Patterson function calculated with ($E^2 - 1$) coefficients. Full-matrix least-squares refinement of the 47 non-hydrogen atoms and difference Fourier placement of the 34 H atoms yielded an R of 0.029 for the 3339 significant data. The molecules are packed in pairs by base stacking and hydrogen bonds between the base and the phosphonate O atoms.

© 1979 International Union of Crystallography

Introduction. Structure determinations of nucleotide analogs in general are useful for the information they yield about the parent compounds. Phosphonate analogs of nucleoside phosphates have been used to study the mechanism of action of phosphatases and phosphate kinases, leading to interest in this group of nucleotide analogs (Myers, Nakamura & Danielzadeh, 1965).

A sample of adenosine 5'-methylphosphonate was supplied by Dr Bimal C. Pal, Biology Division, Oak Ridge National Laboratory, and was recrystallized from a water/ethanol solution in a thermal gradient. The crystallization apparatus was similar to that recently described by Watkin (1972). A specimen $0.35 \times 0.35 \times 0.22$ mm was selected for diffraction study. The space group and approximate cell dimensions were determined from precession and Weissenberg photographs. More accurate cell dimensions were obtained by least-squares refinement with the use of the observed setting angles for ten Mo $K\alpha_1$ reflections, in the range $39 < 2\theta < 43^\circ$, measured with an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). The density of the crystals was measured by flotation in mixtures of chloroform and carbon tetrachloride. Intensity data were collected on the diffractometer with Nb-filtered Mo $K\alpha$ radiation using the θ - 2θ scan technique. Of

3444 reflections with $2\theta \leq 55^\circ$, 3339 were considered observed [$|F_o| > 3\sigma(F_o)$]. Each structure factor was assigned a variance $\sigma^2(F)$ based on counting statistics plus a term $(0.03 F)^2$, empirically derived during refinement. No absorption correction was applied ($\mu = 0.22 \text{ mm}^{-1}$). No significant changes in two standard reflections were observed during the course of the data collection.

The structure was solved from the sharpened Patterson function only after considerable difficulty and with significant assistance from the fast rotation function of R. A. Crowther (ROTRAN; Craven, 1975). The P atom positions were readily determined from the Patterson map, but provided insufficient phasing information to produce a Fourier synthesis significantly different from the Patterson map. It was later found that the positions of the phosphonate O atoms were obscured by extensive vector overlap. The orientation of the adenine rings was found using ROTRAN, with 9-methyladenine (Kistenmacher & Rossi, 1977) as a model search fragment. The self-rotation function confirmed the relative orientations of the adenine rings, which, with packing considerations and assumptions concerning reasonable hydrogen bonding, allowed interpretation of the Patterson map. Successive Fourier syntheses, using $(2|F_o| - |F_c|) \exp(i\phi_c)$ coefficients, completed the deter-

Table 1. *Positional and isotropic thermal parameters* ($\times 10^4$) *for non-hydrogen atoms*

The isotropic temperature factor is $\exp[-8\pi^2 U(\sin \theta/\lambda)^2]$; the values given are the arithmetic averages of the principal components of the anisotropic temperature factors. Standard deviations in units of the last significant digits are given in parentheses.

| | Molecule A | | | | Molecule B | | | |
|-------|------------|-----------|-----------|----------------------|------------|----------|----------------------|----------------------|
| | x | y | z | U (\AA^2) | x | y | z | U (\AA^2) |
| N(1) | 13356 (2) | 4903 (2) | 9742 (3) | 273 (9) | 1570 (2) | 6881 (2) | 1830 (3) | 279 (9) |
| C(2) | 12222 (2) | 4130 (3) | 9434 (3) | 300 (11) | 1092 (2) | 5476 (3) | 2317 (3) | 302 (11) |
| N(3) | 11241 (2) | 4637 (2) | 8360 (3) | 291 (9) | 1672 (2) | 4426 (2) | 3482 (3) | 295 (9) |
| C(4) | 11480 (2) | 6057 (2) | 7555 (3) | 242 (10) | 2843 (2) | 4914 (2) | 4146 (3) | 258 (10) |
| C(5) | 12601 (2) | 6942 (2) | 7741 (3) | 251 (9) | 3414 (2) | 6324 (2) | 3765 (3) | 265 (10) |
| C(6) | 13630 (2) | 6319 (2) | 8912 (3) | 252 (10) | 2706 (2) | 7391 (2) | 2568 (3) | 265 (10) |
| N(6) | 14773 (2) | 6992 (2) | 9248 (3) | 336 (10) | 3098 (2) | 8802 (2) | 2130 (3) | 338 (11) |
| N(7) | 12481 (2) | 8329 (2) | 6697 (3) | 295 (10) | 4609 (2) | 6426 (2) | 4708 (3) | 309 (10) |
| C(8) | 11298 (2) | 8271 (3) | 5918 (3) | 303 (11) | 4748 (2) | 5088 (3) | 5608 (4) | 325 (12) |
| N(9) | 10648 (2) | 6916 (2) | 6372 (3) | 260 (9) | 3716 (2) | 4120 (2) | 5341 (3) | 286 (9) |
| C(1') | 9311 (2) | 6471 (3) | 5810 (3) | 286 (11) | 3621 (2) | 2551 (2) | 6122 (3) | 272 (10) |
| C(2') | 8304 (2) | 7264 (3) | 6419 (3) | 323 (12) | 4597 (2) | 1705 (2) | 5485 (3) | 256 (10) |
| O(2') | 7262 (2) | 6260 (3) | 6938 (3) | 454 (11) | 3984 (2) | 563 (2) | 4716 (2) | 350 (9) |
| C(3') | 7836 (2) | 8320 (2) | 4701 (3) | 260 (10) | 5497 (2) | 1181 (2) | 7176 (3) | 249 (10) |
| O(3') | 6579 (2) | 8765 (2) | 4641 (3) | 342 (9) | 5881 (2) | -248 (2) | 7418 (2) | 352 (9) |
| C(4') | 7973 (2) | 7469 (2) | 3310 (3) | 241 (10) | 4708 (2) | 1223 (2) | 8679 (3) | 279 (11) |
| O(1') | 9154 (2) | 6780 (2) | 3926 (2) | 355 (9) | 3916 (2) | 2408 (2) | 7975 (2) | 380 (10) |
| C(5') | 8040 (2) | 8333 (3) | 1444 (3) | 310 (11) | 5465 (3) | 1482 (3) | 10357 (3) | 355 (12) |
| O(5') | 8986 (2) | 9548 (2) | 1423 (3) | 459 (11) | 6353 (2) | 2753 (2) | 9967 (3) | 441 (11) |
| P | 10000 (0) | 10000 (0) | 0 (0) | 281 (3) | 6647 (1) | 3846 (1) | 11294 (1) | 313 (3) |
| O(6) | 11136 (2) | 10760 (2) | 853 (3) | 412 (10) | 7382 (4) | 5153 (3) | 10325 (3) | 736 (18) |
| O(7) | 10267 (2) | 8623 (2) | -554 (2) | 358 (9) | 5398 (2) | 4089 (3) | 11891 (3) | 503 (12) |
| C(9) | 9229 (3) | 11183 (4) | -1864 (4) | 467 (16) | 7621 (3) | 2889 (4) | 13162 (4) | 489 (18) |
| | | | | Water | | | | |
| | | | | x | y | z | U (\AA^2) | |
| | | | | O(w) | 541 (3) | 1421 (2) | 4017 (3) | 517 (13) |

mination of the structure. The 47 non-hydrogen atoms in the unit cell were refined by full-matrix least-squares methods. During the later stages of anisotropic refinement, the 34 H atoms were located from difference Fourier syntheses alternating with least-squares refinement of non-hydrogen atom parameters, minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The final values of R , the weighted R $\{[\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}\}$, and σ , the goodness of fit $\{[\sum w(F_o - F_c)^2/(n - p)]^{1/2}$, where $n = 3339$ reflections and $p = 423$ variables, were 0.029, 0.043 and 1.16, respectively. The average shift on the final cycle of refinement was 20% of the estimated standard deviation. All refinements were performed with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The final atomic parameters are given in Table 1.*

* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34291 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

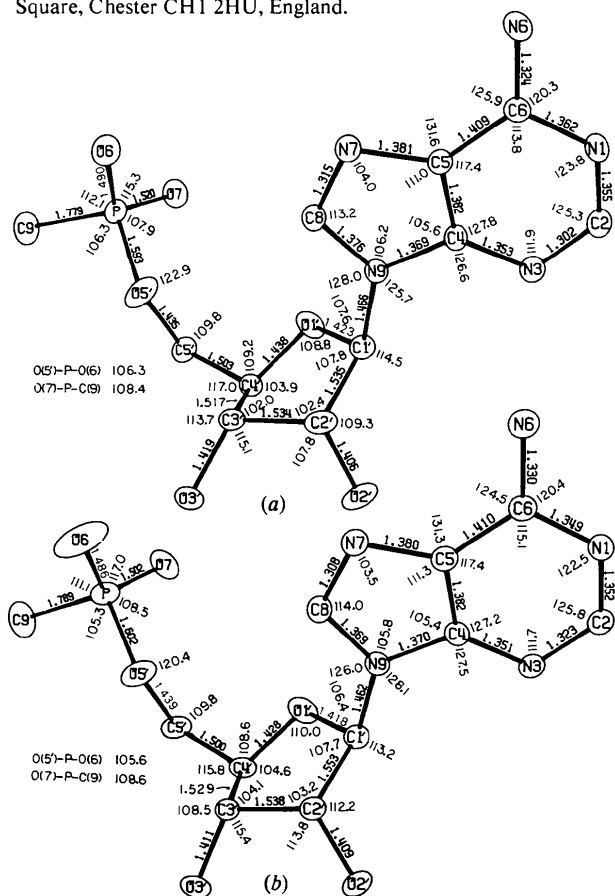


Fig. 1. Bond distances (Å) and angles (°) for (a) molecule A and (b) molecule B. The boundary thermal ellipsoids are drawn at the 30% probability level. The average standard deviation in the bond lengths and bond angles is 0.003 Å and 0.2°, respectively. Illustrations were prepared with the aid of the computer program ORTEP (Johnson, 1965).

Discussion. Drawings of the molecules, including bond distances and angles, are shown in Fig. 1. The conformations of the two independent molecules are nearly identical. Both molecules are zwitterions, with N(1) protonated and the methylphosphonate group ionized. The P—C distances [1.779 (3), 1.789 (3) Å] are consistent with the P—C distance of 1.78 Å found in pyridoxal 5'-methylphosphonate (Cole, Lachmann & Korytnyk, 1972). Other distances and angles are consistent with those determined for other nucleotide structures. Torsion angles descriptive of the molecular conformation are given in Table 2. In both molecules the ribose ring is *anti* relative to the base. The phosphonate ester oxygen, O(5'), is placed *g*⁺ relative to the sugar ring, while the P atom is *trans* to C(4'). Calculation of the pseudorotation parameters (Altona & Sundaralingam, 1972) for the ribose rings reveals the unusual 3_4T and ${}^4_4T^3$ conformations. The conformations of ribose A and B are intermediate between 3'-*endo* and 4'-*exo*, with B very close to 4'-*exo*, an extended conformation with the C(4')—C(5') bond pseudo-equatorial.

The molecules are packed in A—B pairs stabilized by base stacking and base to phosphonate O atom

Table 2. Torsion angles and ribose pseudo-rotation parameters for molecules A and B (°)

| | A | B | |
|----------|-------------------------|-----------|-----------|
| χ | O(1')—C(1')—N(9)—C(8) | 56.5 (3) | 52.9 (3) |
| τ_0 | C(4')—O(1')—C(1')—C(2') | −11.0 (2) | −17.3 (2) |
| τ_1 | O(1')—C(1')—C(2')—C(3') | −13.8 (2) | −3.6 (2) |
| τ_2 | C(1')—C(2')—C(3')—C(4') | 31.6 (2) | 21.2 (2) |
| τ_3 | C(2')—C(3')—C(4')—O(1') | −39.1 (2) | −31.9 (2) |
| τ_4 | C(3')—C(4')—O(1')—C(1') | 31.7 (2) | 31.0 (2) |
| ϕ | P—O(5')—C(5')—C(4') | 136.1 (2) | 143.1 (2) |
| ψ | O(5')—C(5')—C(4')—C(3') | 50.1 (3) | 51.5 (3) |
| ψ' | C(5')—C(4')—C(3')—O(3') | 75.9 (3) | 85.1 (2) |

Ribose pseudo-rotation parameters

| | | | |
|----------|----------------------------|-----------|-------------|
| P | Phase angle from 3_4T | 34.5 | 49.1 |
| τ_m | Magnitude of pucker | 39.2 | 33.1 |
| | Conformational descriptor | 3_4T | ${}^4_4T^3$ |

Table 3. Hydrogen bonds and close contacts of the type D—H...A

| Donor (D) | Acceptor (A) | In molecule at | D—A (Å) | H...A (Å) | \angle D—H...A (°) |
|----------------|----------------|-------------------|-----------|-----------|----------------------|
| N(1) <i>a</i> | O(7) <i>b</i> | 1 + x, y, z | 2.618 (3) | 1.93 | 166 |
| N(1) <i>b</i> | O(7) <i>a</i> | −1 + x, y, z | 2.542 (3) | 1.85 | 174 |
| N(6) <i>a</i> | O(3') <i>b</i> | 1 + x, 1 + y, z | 2.870 (3) | 1.92 | 170 |
| N(6) <i>b</i> | O(6) <i>a</i> | −1 + x, y, z | 2.843 (3) | 2.22 | 162 |
| N(6) <i>b</i> | O(2') <i>b</i> | x, 1 + y, z | 2.902 (3) | 2.21 | 136 |
| O(2') <i>a</i> | O(6) <i>b</i> | x, y, z | 2.601 (3) | 1.88 | 173 |
| O(2') <i>b</i> | N(7) <i>a</i> | −1 + x, −1 + y, z | 2.783 (3) | 2.03 | 172 |
| O(3') <i>a</i> | N(7) <i>b</i> | x, y, z | 2.857 (3) | 2.06 | 169 |
| O(3') <i>b</i> | O(3') <i>a</i> | x, −1 + y, z | 2.750 (3) | 2.06 | 161 |
| O(w) | N(3) <i>b</i> | x, y, z | 2.912 (3) | 2.27 | 142 |
| O(w) | O(6) <i>a</i> | −1 + x, −1 + y, z | 2.837 (4) | 1.94 | 173 |
| C(8) <i>a</i> | O(w) | 1 + x, 1 + y, z | 3.134 (3) | 2.28 | 157 |
| C(8) <i>b</i> | O(2') <i>a</i> | x, y, z | 2.916 (3) | 2.33 | 126 |

hydrogen bonds. Within the pair the stacking distance is about 3.5 Å, the closest contact distances being C(5)*a*...C(5)*b* 3.507 (4), C(5)*a*...N(7)*b* 3.507 (3), C(6)*a*...C(8)*b* 3.433 (4), and C(8)*a*...C(6)*b* 3.453 (4) Å. The stacked bases are oriented so that N(1) and N(6) are near the ionized methylphosphonate group of the paired molecule. N(1)*a*—H...O(7)*b*, N(1)*b*—H...O(7)*a*, and N(6)*b*—H...O(6)*a* hydrogen bonds are present (Table 3), but N(6)*a* is further from O(6)*b* than from O(7)*b* [3.312 (4) versus 3.101 (3) Å], so that only a weak interaction with O(7)*b* is likely. The packing interactions are shown in Fig. 2.

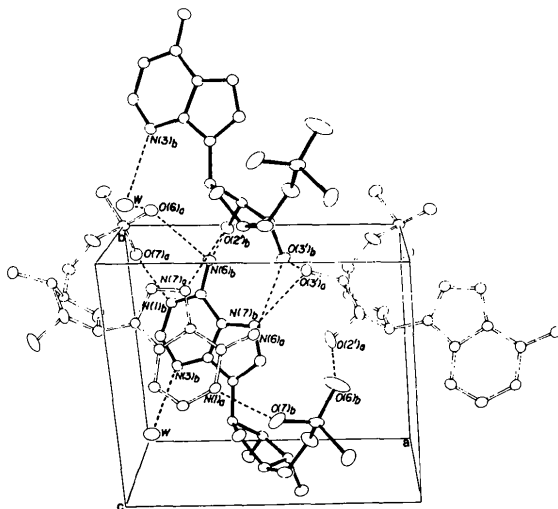


Fig. 2. Packing interactions. Molecule *A* is drawn with hollow bonds. Molecule *B* is drawn with solid bonds. The dashed lines represent hydrogen bonds. The thermal ellipsoids are drawn at the 30% probability level.

Adjacent *A*–*B* pairs are held together by stacking forces [stacking distances about 3.3 Å: N(1)*a*...C(2)*b* 3.458 (3), C(2)*a*...C(2)*b* 3.221 (4), C(2)*a*...N(3)*b* 3.360 (4), N(3)*a*...C(2)*b* 3.384 (4) Å, closest contacts] and an intricate network of hydrogen bonds, including interactions at position N(7) of both adenine rings. The water molecule participates as a donor in hydrogen bonds to N(3)*b* and O(6)*a*. Both C(8)–H groups are involved in close contacts: C(8)*a*...O(*w*) 3.134 (3), C(8)*b*...O(2')*a* 2.916 (3) Å.

Data collection at Oak Ridge National Laboratory was sponsored by the Division of Basic Energy Sciences of the Department of Energy under contract with Union Carbide Corporation.

References

- ALTONA, C. & SUNDARALINGAM, M. (1972). *J. Am. Chem. Soc.* **94**, 8205–8212.
- BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1968). Report ORNL-4143. Oak Ridge National Laboratory, Tennessee.
- COLE, F. E., LACHMANN, B. & KORYTNYK, W. (1972). *J. Heterocycl. Chem.* **9**, 1129–1131.
- CRAVEN, B. M. (1975). ROTRAN, Department of Crystallography, Univ. of Pittsburgh, Pittsburgh, Pennsylvania.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KISTENMACHER, T. J. & ROSSI, M. (1977). *Acta Cryst.* **B33**, 253–256.
- MYERS, T. C., NAKAMURA, K. & DANIELZADEH, A. B. (1965). *J. Org. Chem.* **30**, 1517–1520.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WATKIN, D. J. (1972). *J. Appl. Cryst.* **5**, 250.

Acta Cryst. (1979). **B35**, 1727–1729

Structure of *p,p'*-Ditolyl Ditelluride

BY M. R. SPIRLET, G. VAN DEN BOSSCHE, O. DIDEBERG AND L. DUPONT

Laboratoire de Cristallographie, Institut de Physique B5, Université de Liège (au Sart Tilman), B-4000 Liège, Belgium

(Received 20 November 1978; accepted 27 March 1979)

Abstract. C₁₄H₁₄Te₂, orthorhombic, *Pbc*2₁, *a* = 8.305 (3), *b* = 26.329 (6), *c* = 6.439 (3) Å, *Z* = 4. The structure was determined by three-dimensional X-ray analysis. Positional and temperature-factor parameters for Te and C atoms have been refined by block-diagonal least-squares methods to a final *R* value of

0.057 for 1873 observed reflections. The Te–Te bond length of 2.697 (3) Å and the other observed intramolecular distances and angles are all consistent with the accepted values from earlier investigations. The value of the dihedral angle C–Te–Te/Te–Te–C is 85.7 (4)°.

0567-7408/79/071727-03\$01.00

© 1979 International Union of Crystallography