# The Structure of 1-(4-Imidazolylsulfonyl)-4-phenylimidazole

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The crystal and molecular structures of 1-(4-imidazolylsulfonyl)-4-phenylimidazole have been determined by single-crystal X-ray techniques. Crystals are orthorhombic, space group *Pbca*, with a =9.808 (6), b = 7.351 (5), c = 33.958 (12) Å, and Z = 8. The structure was solved by direct methods and refined by least-squares calculations to an *R* of 0.058 for 1038 reflexions with  $F > \sigma(F)$  measured on a diffractometer. The molecules form chains in one dimension linked by asymmetric N-H···N hydrogen bonds with N-H of 0.93 Å, H···N of 1.94 Å, N-N of 2.866 Å, and N-H···N of 172°. The chains are associated in the second dimension by the stacking of parallel bases separated by 3.41 Å.

#### Introduction

The present X-ray study was initiated to establish the molecular structure of the title compound as a guide to our synthesis program on imidazole derivatives. We were particularly interested in the point of attachment of the phenyl ring, the tautomeric form of the imidazoles, and the nature of the hydrogen bonding.

#### Experimental

A sample of 1-(4-imidazolylsulfonyl)-4-phenylimidazole was obtained from Dr Ellis of this laboratory. Crystals suitable for X-ray work were obtained by the slow evaporation of an ethyl acetate solution. Crystals were air stable. Crystals are orthorhombic; the space group was uniquely determined from the systematic absences observed on Weissenberg and precession photographs. Cell parameters were obtained from the least-squares refinement of the angular positions for 10 reflections carefully centered on a diffractometer at room temperature. The cell data are summarized in Table 1.

| Table I. Crysta | ıl a | iata |
|-----------------|------|------|
|-----------------|------|------|

| $C_{12}H_{10}N_4SO_2$ |                          |
|-----------------------|--------------------------|
| Space group           | Pbca                     |
| a                     | 9.808 (6)                |
| b                     | 7.351 (5)                |
| с                     | 33.958 (12)              |
| Cell volume           | 2448·3 Å <sup>3</sup>    |
| Ζ                     | 8                        |
| $\rho$ (calculated)   | $1.49 \text{ g cm}^{-3}$ |
| o(observed)           | $1.49 \text{ g cm}^{-3}$ |
| μ                     | 2.68 cm <sup>-1</sup>    |
|                       |                          |

A prismatic crystal of dimensions  $0.13 \times 0.30 \times 0.20$ mm was chosen for data collection. The crystal was mounted on a Picker four-circle automatic diffractometer with the *b* axis along the diffractometer  $\varphi$  axis. The data were measured with Zr-filtered Mo radiation (Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å) and the  $\theta - 2\theta$  scan technique. The scan range for each reflection was  $1.5^{\circ}$  plus the  $K\alpha_1 - K\alpha_2$  separation; backgrounds of 15s were measured before and after each scan. 1140 reflections were measured out to  $40^{\circ}2\theta$ . No crystal decomposition was observed from the periodic recording of standard reflections.

The data were corrected for Lorentz and polarization effects, but not for absorption. The structure factor errors were estimated according to a scheme reported earlier (Guggenberger, 1968). Those data with  $F < \sigma(F)$ were given zero weight in the final refinements. A special effort was made to examine each reflection for possible overlap from neighboring reflections due to lack of resolution with Mo radiation caused by the large c cell edge. Each reflection was individually scaled and plotted as it was measured (on-line to Calcomp) along with the background approximation for that reflection. On examination it appeared that 46 reflections might involve some overlap; these fell in the class  $h \le 2$ ,  $k \le 4$ , and l > 10. These data were remeasured with a  $2\theta$  scan range of  $0.80^\circ$ . Now 21 of these were acceptable, but there was still some question about the remaining 25 reflections so they were excluded entirely from the refinement. A structure-factor comparison was made at the end of the refinement for the 21 reflections included and their agreement was acceptable.

#### Structure determination and refinement

The positions of the nonhydrogen atoms were determined by the symbolic addition procedure with the Fleischer, Dewar & Stone (1967) computer program. The statistical distribution of E's followed the expected centric distribution; the observed values of 0.81 for  $\langle |E| \rangle$  and 0.95 for  $\langle |E^2 - 1| \rangle$  are close to the theoretical values of 0.798 and 0.968, respectively (Karle, Hauptman & Christ, 1958). 278 reflections were phased in the  $\sum_2$  process (E's > 1.0 used). Three reflections were

# Table 2. Final coordinates and thermal parameters for the heavy atoms

Standard deviations are given in parentheses. Temperature factor has the form exp  $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . Data are  $\times 10^4$  (\*  $\times 10^5$ ).

|             | x                 | У           | Z           | $\beta_{11}$ | $\beta_{22}$     | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|-------------|-------------------|-------------|-------------|--------------|------------------|--------------|--------------|--------------|--------------|
| S           | 45206 (13)*       | 61520 (19)* | 41310 (4)*  | 804 (18)*    | 1539 (33)*       | 73 (2)*      | 15 (21)*     | 39 (4)*      | 0 (6)*       |
| <b>O(1)</b> | 5686 (3)          | 5340 (5)    | 43100 (11)* | 76 (4)       | 229 (10)         | 110(4)*      | 51 (5)       | 47(11)*      | 74 (17)*     |
| O(2)        | 3707 (3)          | 5258 (5)    | 38495 (10)* | 118 (5)      | 192 (9)          | 90 (4)*      | -31(6)       | 20 (12)*     | -95(17)*     |
| N(1)        | 5101 (4)          | 8037 (6)    | 39123 (12)* | 79 (6)       | 183 (11)         | 71 (5)*      | -15(7)       | 17(13)*      | 34 (20)*     |
| N(2)        | 6331 (5)          | 10513 (7)   | 38089 (15)* | 111 (7)      | 200 (13)         | 134 (6)*     | -31(7)       | -76(18)*     | 156 (24)*    |
| N(3)        | 1712 (4)          | 7575 (6)    | 48612 (12)* | 79 (6)       | 172 (11)         | 72 (5)*      | 7 (6)        | 53 (14)*     | 34 (20)*     |
| N(4)        | 3969 (4)          | 7567 (5)    | 48495 (12)  | 78 (6)       | 164 (11)         | 69 (5)*      | -13(6)       | 17 (14)*     | 9 (19)*      |
| C(1)        | 6 <b>2</b> 40 (6) | 9012 (9)    | 40083 (17)* | 95 (8)       | <b>220</b> (16)  | 109 (7)*     | -31(10)      | -69(18)*     | 92 (29)*     |
| C(2)        | 5183 (5)          | 10574 (7)   | 35664 (15)* | 78 (7)       | 154 (14)         | 71 (6)*      | 1 (9)        | 59 (18)*     | -50(26)*     |
| C(3)        | 4422 (5)          | 9084 (8)    | 36337 (15)* | 87 (7)       | 188 (14)         | 63 (6)*      | 5 (9)        | -22(16)      | 52 (25)*     |
| C(4)        | 2875 (6)          | 7970 (7)    | 50575 (15)* | 79 (7)       | 191 (14)         | 71 (6)*      | -21(9)       | 26 (20)*     | 71 (23)*     |
| C(5)        | 3454 (5)          | 6929 (7)    | 44985 (15)* | 59 (7)       | 133 (12)         | 77 (6)*      | -1(7)        | 1 (16)*      | 30 (22)*     |
| C(6)        | 2065 (5)          | 6916 (7)    | 45007 (16)* | 84 (8)       | 156 (13)         | 82 (6)*      | 4 (8)        | 19 (17)*     | 47 (23)*     |
| C(7)        | 4968 (6)          | 12053 (8)   | 32875 (15)* | 96 (8)       | 177 (14)         | 73 (6)*      | 24 (9)       | 47 (18)*     | $6(25)^*$    |
| C(8)        | 3753 (6)          | 12152 (8)   | 30780 (16)* | 134 (9)      | 202 (15)         | 77 (6)*      | 46 (9)       | 4 (20)*      | 35 (28)*     |
| C(9)        | 3538 (6)          | 13539 (10)  | 28068 (18)* | 124 (8)      | <b>2</b> 68 (18) | 98 (7)*      | 37 (11)      | 54 (20)*     | 3 (31)*      |
| C(10)       | 4545 (9)          | 14832 (10)  | 27460 (20)* | 179 (11)     | 316 (21)         | 111 (8)*     | 96 (14)      | 101 (27)*    | 174(34)*     |
| C(11)       | 5729 (7)          | 14766 (9)   | 29621 (21)* | 173 (11)     | 209 (16)         | 129 (9)*     | 3 (11)       | 147 (26)*    | 121 (35)*    |
| C(12)       | 5945 (6)          | 13386 (9)   | 32296 (17)* | 122 (8)      | 227 (16)         | 96 (7)*      | -3(11)       | 54 (19)*     | 68 (28)*     |

assigned symbols and three were used to fix the origin. All the nonhydrogen atoms were found on the resultant E map.

The model was refined by full-matrix least-squares calculations with isotropic thermal parameters giving an  $R (= \sum ||F_o| - |F_c|| / \sum |\dot{F}_o|)$  of 0.115 and  $R_w \{= [\sum w(|F_o| - |F_c|)^2 / w |F_o|^2]^{1/2} \}$  of 0.133. The model was refined with anisotropic thermal parameters giving an R of 0.088 and  $R_{w}$  of 0.096. At this point electron density maps were calculated through the planes of the imidazole and benzene rings to locate the hydrogen atoms. All the hydrogen atom positions were located easily and included in the refinement; fixed isotropic thermal parameters of 4.0 Å<sup>2</sup> were used for the imidazole hydrogens and 5.0  $Å^2$  for the benzene hydrogens. The final refinements were done in two sections: (a) all nonhydrogen atom parameters, and (b) the parameters involving the hydrogen atoms. The final R values for the 1038 reflections with  $F > \sigma(F)$  are 0.058 for R and 0.060 for  $R_w$ . The corresponding values for all the data (1114) reflections) are 0.067 for R and 0.061 for  $R_w$ . The final goodness-of-fit  $\{ = [\sum w ||F_o| - |F_c|]^2 / (m-n) \}$  is 1.35.

The scattering factors for the neutral atoms were used (Hanson, Herman, Lea & Skillman, 1964). The sulfur atom was corrected for the real and imaginary parts of the anomalous scattering effect (Templeton, 1962). A final electron-density difference map was calculated and showed no unusual features ( $|\varrho| \le 0.2$  e Å<sup>-3</sup>).

The final parameters for the heavy atoms are given in Table 2 and those for the hydrogen atoms in Table 3; the hydrogens are identified also by the atoms to which they are attached. The observed and calculated structure factors are listed in Table 4.

# Table 3. Coordinates and thermal parameters for the hydrogen atoms

|            | x      | У      | Z      | В   |
|------------|--------|--------|--------|-----|
| H(1)N(3)   | 0.0839 | 0.7622 | 0.4968 | 4·0 |
| H(2)C(1)   | 0.6797 | 0.8540 | 0.4205 | 4.0 |
| H(3)C(3)   | 0.3533 | 0.8610 | 0.3505 | 4·0 |
| H(4)C(4)   | 0.2821 | 0.8392 | 0.5328 | 4.0 |
| H(5)C(6)   | 0.1418 | 0.6542 | 0.4322 | 4·0 |
| H(6)C(8)   | 0.2977 | 1.1164 | 0.3155 | 5.0 |
| H(7)C(9)   | 0.2604 | 1.3538 | 0.2649 | 5.0 |
| H(8)C(10)  | 0.4408 | 1.5678 | 0.2600 | 5∙0 |
| H(9)C(11)  | 0.6437 | 1.5664 | 0.2954 | 5.0 |
| H(10)C(12) | 0.6797 | 1.3261 | 0.3378 | 5.0 |

#### Discussion

### Molecular structure

The molecular structure illustrating the numbering system used here and the thermal ellipsoids plotted at the 50% probability level is shown in Fig. 1. Two points of significant interest to us are established immediately, namely, the point of attachment of the phenyl ring and tautomeric form of the N(3), N(4)imidazole ring. The phenyl ring is attached to C(2) instead of the other possibility for attachment to C(3). The N(3), N(4)-imidazole ring exists as the N(3)-H tautomeric form as opposed to the N(4)-H form.

The bond distances are shown in Fig. 2 and the bond angles in Fig. 3. In both figures the open bonds signify the double-bond positions of the primary resonance form. Other short intramolecular distances as well as intermolecular distances are given in Table 5. A comparison of imidazole bond distances with some observed structures is given in Table 6 which shows the similarities of imidazole geometries in very different bonding situations, including the metal-bonded case. Further comparisons are available for imidazole geometries in purines (Sletten & Jensen, 1969) and adenines (Watson, Sutor & Tollin, 1965) and metal-imidazoles (Mighell & Santoro, 1971; Prout, Allison & Rossotti, 1971).

The S-O distances are in the range of frequently observed values (Meyers & Trueblood, 1969, and refer-

### Table 4. Observed and calculated structure factors

The columns give the running index h,  $10F_o$ , and  $10F_c$ . An asterisk marks an unobserved reflection (see text).

|                     | 4.6. 2. 2         | • 2 13•         | 5 172 /56                  | 1 245 234     | 4 144 145     | 2 2 3 3 2 7 5 | , 354 324   | • 122 ••                                  | 1 149 190       | 2.22        |             |
|---------------------|-------------------|-----------------|----------------------------|---------------|---------------|---------------|-------------|---|-----------------|-------------|-------------|
| 22"032174           | 213141333         | A P             | 6 168 189                  | 2 274 247     | 4. 0.13       | 1 110 111     | 8 482 485   | 2.1                                       | 2 342 34        | 1 1 1 1 1 1 | 1 10 101    |
|                     | 1 924 935         | 12:332134       | 1 12 12                    | 2 424 444     |               | 2             |             |   |                 |             | 1 101 11    |
| • • • • • • • • • • | 2 202 202         | 1               |                            |               |               |               | 1 11 11     |   |                 | 4.1 4.21    | 4.45        |
|                     | 1 1 1 1           | 1 10 10         |                            | 4 321 314     |               |               | 1 212 224   | 5 616 479                                 | 5.1. 9.18       | 1 41 44     | 2 346 352   |
| 2 164 181           | 4 107 114         | 5 1 8 1 8       | 1 954 952                  | 7 321 327     | 4 315 341     | 4 3: - 291    | 4 144 144   | 4 174 174                                 | 1 237 240       | 2 4 17      | \$ 75 45    |
| 4 444 454           |                   | 4 113 112       | 2 287 258                  | 4 249 244     | 5 313 318     | 7 11-         | 5 384 395   | 5 42 34                                   | 2 154 169       | K.L. 0.22   | 2 44 54     |
| 6 264 265           |                   | 7 242 253       | 3 141 145                  | 9 196 201     | 4 140 151     | \$ 312 324    | 6 324 3:4   | a 57 31                                   | 3 139 157       | 8 428 419   | *·L* 0·24   |
| 4 32 36             | 4 144 175         | 8 318 315       | 4 14 14                    | 4             | 1 2*3 315     | 4* 1-12       | 7 267 276   | , ,, ,,                                   | 4 38 24         | 1 249 249   | 0 0 120.    |
|                     |                   | 9 41 52         | 5 337 324                  | 3 448 482     | 8 89 102      | 3 341 314     | 8 47 31     | 4   | A               | 2 144 142   | 1 301 243   |
| 1 352 363           | 4                 |                 | a 232 22a                  | 5 375 314     | 44.47 1417    | 2 3:4 316     | ** 7.14     | : 3:5 2**                                 | 1 103 157       | 3 33 39     | 2 12/ 120   |
| 21 : 191022         | 1 714 728         | 317551784       | , 36 43                    | 3 452 443     | 244 234       |               | : 342 747   | 2 : 34 : 27                               | 2 141 130       |             |             |
| * 10* 18*           | 2 100 100         | 1 443 436       |                            |               | 1 100 100     | 4 318 354     | 1 1 1 1 1 1 | · · · · · · · ·                           | 1 1 1 1 1 1     |             | 1 111 101   |
|                     | 3 3 7             | 2 4/4 4/4       | 1.11.11                    | 2             |               | 2             | 1 1 1 1 1   |   | 1 10 12         |             | 1.1.1 1.24  |
| 1 1 2 4 1 4 1       |                   | 1 111 112       |                            | 1 4 4         |               |               | 1           |   | A 147 345       | 2 197 199   | 2 112 170   |
|                     |                   |                 | 112.021                    | 1 3 12 334    | 4 427 432     |               | S (## 188   | 7 134 114                                 | 7 124 109       | 3 07 120    | 3 113 94    |
| 1 61 61             | 1 141 101         |                 | 2 190 184                  | 1 1 24        | 1 108 135     |               | 4 32 23     | 4   | 8.1.4 2.19      | 4 244 259   | 4 256 247   |
| 1 1 1 1 1 1         | 4 221 233         | 1 10 37         | 3 587 354                  |               | 4 324 321     | 0 742 741     | 1 10 102    | : 443 475                                 | 3 337 374       | 5 153 183   | 9 242 257   |
|                     |                   | 4 32            | 4 148 158                  | C 2+2 25*     | **** 2.13     | 1 33 34       | 4 5 53+     | 1 117 114                                 | 1 74 14         | 6 281 270   | 4           |
| 4.4.2               | 0 235 230         | 41. 2 3. 4      | 5 177 177                  | 1 338 348     | 0 304 312     | 2 11 105      | A.L.P. 3-34 | 2 :53 :44                                 | 2 241 302       | s 2.22      | C 214 242   |
| - 343 368           | 1 37 28           | 1 505 524       | • 535 534                  | 2 45 40       | 1 112 11*     | 3 144 144     | 1 374 358   | 3 344 377                                 | 5 156 125       | 0 244 245   | 2           |
| 2 14, 502           | 2 432 444         | 2 475 738       | 2 2 13.                    | 3 121 11      | 2 2 2 2 2 2   | 1 122 102     | 1 1 1 1 1   | 1 122 133                                 | 1 111 122       | ( () ()     | 1.3.3       |
| 4 200 277           | 3 318 323         | 3 140 130       | 1 1 . 2                    |               | 2 10 10       | 2 10 10       | 1 100 100   |   |                 | 1 245 254   | 4 139 144   |
| * 12* 11/           |                   | *               |                            | 2 240 270     | 1 1 1 1 1     | 1 1           | 1 11 11     |   |                 | 9 124 123   | 1.1. 3.20   |
|                     | 2                 | 1               | 1 7 6.                     | 1             | 1 1 1         | 1 10 100      |             | 1 144 144                                 | 3.1             | 1 1 1 1     | 2 104 124   |
| 1 2 4 1 44          | 7 421 421         | 7 323 322       | 3 45 47                    | · 302 311     | 5 42 34       | 4 3.12        | 7 0 34+     | 3 35 45                                   | 2 231 240       | 8.44 3.22   | 3 141 149   |
| \$ 252 258          | 5.1.5 5. 2        | 1 12 15         | 4 334 322                  |               | 1 37 2        | 1 155 145     | 4.4.4.14    | , 22 )                                    | 3 142 144       | 2 74 85     | 4 55 52     |
| 4                   | 1 176 183         | 6.27 6. 6       | 3 344 343                  | 1 487 493     | 4* 3.10       | 2 14: 179     | 7 20 0      | 4 3 28+                                   | 4 245 254       | 3 432 437   | C.L. 4.28   |
| 3 2 424             | 2 77 47           | 3 732 743       | • 371 323                  | 2 263 249     | 1 111 441     | 2 55, 522     | 3 55 63     | *-L* *-1*                                 | 1 1 1 1 1 1 1 1 |             | 100 102     |
| 2 15 131            | 3 200 215         | 1 47 40         | 7 125 114                  | 3 147 147     | 2 224 25?     | 1 111 111     | 1           | ?   | 1.11            | 2.22.24     | 1 1 1       |
|                     | 1.11.2            | 1 82 82         | 1.22.17                    | 1.11.12       |               | 2 14 15       |             |   | 203 200         | 0 340 38    | 1.1. 1.75   |
|                     | 7 1/2 104         |                 |                            | 1 2 3         |               |               | 2 2         |   | 1 125 31        | 1 256 250   | 2 334 333   |
| 1                   | 1 1 1 1 1 1       |                 | 1 11 12                    | ; ;; ;i       |               |               | 1 15 12:    | 2 424 585                                 | 2 114 124       | 2 323 329   | 3 145 140   |
| 1.21.21             | 278 264           | 4 134 154       | 2 110 105                  | 4 227 194     | 1 21.         | 2 465 467     |             | 3 221 211                                 | 3 134 155       | 3 239 243   | 4 247 244   |
|                     | 37 37             | 7 226 234       | 1 1 12                     |               | 4 239 224     | 444 441       | 1 11 12     | 4 334 325                                 | 4 429 435       | 4 40 100    | 5 40 87     |
| 5 394 391           | 2 92 131          |                 | 4 74 16                    | 3 467 428     | 4-12          | 2 384 344     | 2 2 15*     | 5 141 144                                 | 5 48 67         | 4.1.4 9.22  | 4.1. 2.27   |
| . 101 105           | 3 140 127         | 3 2 32*         | 9 42 131                   | 7 325 374     | 3 1 33        | 3 319 324     | 3 154 154   | • • •                                     |                 | 1.0.2       | 2 4 2 4 2 6 |
| 7 294 314           | 4 127 141         | 2 80 196        | o <b>o</b> oo              | 2 : •2•       | 1 275 244     | • : 22+       | 4 49 22     | 1 1 1 1 2 2                               | 1 12 120        | 2 141 101   | 1 1/2 12    |
| 4 13: 133           |                   | 3               | 7 112 114                  | 3 4 3 3 3 4 3 | 1 222 222     | 3 204 205     | \$ 114 187  |   |                 |             | 1 1 1 1 1 1 |
| • 35• 355           | 1 201 272         | 220 21          |                            | 112 122       |               | 1 1 1 1 1     |             |   |                 | 1 11 1      | 5.27        |
|                     |                   | 1 11 11         | 1.1.1.1.1                  |               | 1 397 344     |               | 1 1 1 1 1 1 | 2   | 2 22 34         | 3 201 203   | 2 30 9      |
|                     |                   |                 | 1 10 10                    | 2 241 242     |               | 3 397 420     | 1 1 1 1     | 3 294 299                                 | 1 33 41         | 4 171 199   | 5 52 10     |
| 2 243 243           | 1 414 411         | 6 73 94         | 4 422 424                  |               | 1 231 207     | 3 17' 120     | 4.4.4 2.29  | 4 42 42                                   | 2 343 348       | 3 101 111   | 4-6* 0-20   |
| 3 435 476           | 4 64 66           | 1 172 74        | 1 3 1.                     | 1 153 190     | 4             | 4 1 2 1 34    | 1 11 109    | 3 398 393                                 | 3 344 314       | 4 143 149   | 2 216 221   |
| 4 311 329           | 5 235 223         | 2 108 117       | + 23¢ 223                  | 2 443 452     | ; 3 7.        | 5 64 45       | 2 *3 7:     | 4 44 41                                   | 4 123 125       | K.L. 2.23   | 1 343 342   |
| 5 142 158           | · 207 201         | 3 2 40          |                            | 3 183 198     | 2 24 23       | 4.1.4.4.12    | 3 60 35     | 7 103 100                                 | 5 740 743       | 0 142 192   | 2 +4 101    |
| a 114 118           | 7 254 195         | 4 :54 127       | 0 137 119                  | 4 274 247     | 1 72 14       | 2 24: 244     | 4 359 344   | ** 3·1/                                   | 4               | 2 124 144   | , , , , , , |
| ,                   | 4 277 244         | 81.0.21.9       | 1 12 55                    | 5 128 156     |               | 1 101 100     | 5 12 13     |   | 1 3/4 3/3       | 3 303 30    |             |
| 1.22.11             | 47 23             | 1 22 222        | 1.11.11                    | 12 11         | 1 112 265     |               |             | 5 346 344                                 |                 | 5 344 342   |             |
|                     |                   | 1 246 247       | 1 10 10                    |               | 4.1.4 4.13    |               | 1 121 14    | 4 134 124                                 | 2 105 17        | 4 94 55     | 2 114 100   |
|                     | 21 22 1 20 1 20 1 |                 |                            | 1 143 144     | 147 147       | 189 184       |             | 5 241 267                                 | 3 22 32         | 8-1.* 3-23  | 3 293 289   |
|                     | 1 122 141         | 5 . 07          | 121932278                  | 2 65 10       | ·             | 3 492 474     | 2 2 21      | \$ 259 274                                | 4 159 156       | 1 346 303   | + 243 252   |
| 1 1 44.             | 1 74 42           | 4 192 192       | 216771082                  | 3 40 44       | 2 12 111      | 3 3: 7 312    | 1 324 314   | 2 5 44+                                   | 5 239 232       | 2 43 44     | 4. 4 2.24   |
| 4 122 113           | 4 34 44           | 7 259 257       | 3 846 824                  | 4 105 105     | 3 100 104     | * 337 363     | 2 744 774   | A 4 . 4. 17                               | • '• '>         | 3 48 27     | 1 1 1 1 1 1 |
| 5 152 158           | > •* •1           | 101 102         |                            | K             | 4 144 134     | 5 54 15       | 3 443 493   | 2 102 134                                 | 7 143 159       | 224 234     | 1 1 20      |
| + \$10 \$03         | 0 755 725         | + 202 1.07      | 5 76 13                    | 1 110 222     |               | 4 334 342     |             | 1 10 102                                  |                 |             | 4 1 12 134  |
| 1 1 2 111           | 144 167           |                 |                            |               | 1 1 1 1 1 1 1 |               |             | 1 274 241                                 | 1 139 132       | 0 261 245   | 3.20        |
| 1 21. 11            | 1 22 22           | 1 111 111       |                            | 4 199 197     | 1 114 141     |               | 1 127 12    | 1 12 23                                   | 2 193 174       | 2 175 175   | 2 174 144   |
|                     | 1. 1              | 2 144 144       | 4 3.4 314                  | 5 146 177     | 4 114 11      | 1 1 1120      | 41.4 3.19   | 5 28 34                                   | 3 239 230       | 3 62 62     | 4-6* 1-29   |
|                     | 201 251           | 2 441 241       |                            |               | 5 6 9         | 342 345       | 1 108 **    |   | 4 3 37+         | 4 141 173   | 1 337 320   |
| 2 174 124           | 2 117 121         | 4 2 234         | 3 144 114                  | 2 24 44       | . 335 325     | 5             | 2 428 417   | 4.4. 5.57                                 | 2 12 12         |             | 2 100 100   |
| 3 8-1 814           | 3 244 245         | 3 271 264       | 1 413 403                  | 144 137       | 7 334 241     | 1 10 12       | 3 1 2 20    | 1 1/2 100                                 |                 |             | 1 107 233   |
|                     |                   | • 6. 6.         | 1                          |               |               |               | 1 210 242   | 1 1 1                                     | 1 147 474       | 3 53 1      | 1.1. 2.29   |
|                     | 1.3.4             |                 | 1 3 4 3 3                  |               |               | 124 11        | 122 125     | ·   | 2 66 37         | 3 342 344   |             |
|                     |                   |                 | 1 11 11                    |               |               | 1 145 155     | 3 200 305   |   | 3 267 261       | 4 214 212   | 1 124 140   |
|                     |                   | 1 1 1 1 1 1 1 1 | 4 142 314                  | 3 2:4 220     | 2 424 547     | 8 233 284     |             | 0 2 14*                                   | 4 100 135       | 5 242 235   | 3 .41 .48   |
| 1 1 1 1 1 1         |                   | 2 433 408       | 7 367 371                  | 4 235 244     | 311371141     | 4             | 0 135 124   | A   | 5 233 237       | 4 85 54     | 3 100 102   |
| 2 1** 201           | 3 445 418         | 3 303 288       | 4 245 225                  | 5 274 274     | 5.5 305       | 1 338 324     | 1           | 2 422 462                                 | 0 110 03        |             |             |
| 1 15. 25,           | 1 11 12           | 204 217         |                            | 130 110       |               | 1 1 1 1 1 1   |             |   |                 |             |             |
| 2 10 122            | 2 +00 +23         | 2 12 12         | 1 122 122                  | i?            |               | 2 7 22.       |             | ( " . · · · · · · · · · · · · · · · · · · | 244 24          | 1 12 12     | 6 444 481   |
| 1 11 11             | 1 1 1 1           | 2 22 214        | 1 144 114                  |               | \$7 39        | 3 34 41       | 3 34        | 4 191 199                                 | 2 111 45        | 5 340 374   | 5 148 144   |
|                     |                   |                 | 2 237 254                  | 1 350 324     | 4. 4. 1. 1.   | \$ 339 325    | 4 139 142   | 5 284 278                                 | 3 365 343       | 4 119 146   | 2 45 5      |
| 1 2:1 203           | 4 9 44*           |                 | 47 100                     | 2 407 415     | 1 . 25 . 47   | 7 13: 191     | 4           | \$ 376 370                                | • • 21          | E.L. 2.24   | 3 234 236   |
| 1 12 1 1 1          | 7 54 57           | 0 370 394       | • 2*1 2#3                  | 3 . 5 . 1+    | 2 273 249     | 4.13          | 1 242 253   | 1 169 102                                 | > 202 194       | 0 0 11      |             |
| 2 125 129           |                   | 1 134 128       | 2 111 114                  | • >2> >10     | 2 222 232     | 7 122 100     | 1 (2) (2)   | 1.1.1                                     |                 | 1           | 1. 19. 13   |
| 3 23 293            | 1 47 22           | 2 244 274       | 40 2                       | 107 11        | 1 133 152     |               |             |   |                 | :           |             |
|                     | 6 111 122         | 1 122 14        |                            |               | 1 15 16       |               |             | 3.00.00                                   | 3 12 1          | 2 2 3 2 2 3 | 1           |
|                     | 1 1 1 1 2 7       | 101 1           | 1 207 202                  | . 102 140     | 7 405 397     | 4 12          |             |   | 4               | 5 256 267   | 4 4 4 4 4   |
|                     | 5 30 11           |                 | 1 13 14                    |               | 4             | 1 121 105     | 3 479 442   | 3 202 191                                 | 1 362 343       | 4 3.24      | 1 41 30     |
| 1,112,121           |                   | 1 30 12         | 3 200 1 3                  | 6 47 41       | 2 475 126     | 4 35 71       | 1 .9 1      | 4 431 428                                 | 2 150 190       | 2 237 219   | 2 247 249   |
| 584 636             | 4.64.3            |                 | 4 110 ice                  | 1 416 410     | 1 341 375     | 4 5.13        | 2 10 15     | 1 1 1 2 2                                 | 2 21 4          | 3 100       |             |
| 2 4/2 413           | : 1 12*           | 1 200 213       | 2 141 142                  | 1 11**        | 1 11 11       | 1 129 129     |             |   |                 |             |             |
| 3 .47 147           | 1 111 109         | 2 121 121       | • 12• 333                  |               | 1 1 2         | 1 12 12       | 2.4         | 1 10 22                                   |                 |             |             |
| 1 112               | 2 244 244         | 2 (11 (12)      | 1.2 170                    | 10.10         |               | 1             |             |   | ,               | 5 253 305   | 374 347     |
| 2 10 10             |                   | 10. 11.         |                            |               |               | 1 12 1 1      | 5 5 6 55    | 3 102 3-1                                 |                 | 1 47 10     | 1 100 100   |
| 1 1 1               |                   | 6 Hi 155        |                            | , , ,,        | 7 165 17      |               | 4 434 421   | 4 319 325                                 | : 154 203       | 2 243 252   | 4           |
| 4 245 204           | 1 211 274         |                 | 3 124 141                  |               | 4             | 6 300 300     |             | 5 11 11                                   | 2 415 414       | 3 16 13     | 1 1 4 1 1 1 |
| 1 100 110           |                   | 0 174 174       | 4 64 65                    | 1 4 44        | 1 31: 382     | 276 278       | 6 126 128   | 1+2 1 <sup>2</sup> 1                      | 3 2:4 218       | K.L.* 1.25  |             |
| 4.5 4. 2            | 711791113         | 1 44 100        | 5 44 A                     | 2 339 342     | 2 87 59       | 2 133 143     |             | 2 32 4                                    | 4 3 2 242       | 1 . 11 . 22 |             |
|                     | \$ 540 574        | 2 301 243       | <ul> <li>34, 13</li> </ul> | 3 75 44       | 3 331 341     | 3 244 224     |             |   | 2 22 22         | 2 112 120   |             |
| 2 424 422           | 218341874         | 3 469 370       | 5 A                        | 1 400 412     | 1.11.11       |               |             | 1 10 10                                   |                 |             |             |
| 1 121 241           | 3 194 205         |                 | 5 336 340                  |               |               | 1 1 1 1       | 24          |   |                 |             |             |
| 1 1 2               | 1 133 123         |                 | ; ; ; ; ; ;                |               |               | 2 2 4 2       | 3 15 15     | 1 11 11                                   | 3 300 200       | 0 361 360   |             |
|                     |                   | 111411145       | 3 2 4 5 2 4 7              | 3 375 346     | 1 205 200     | 3 414 443     | 4 364 338   | s 233 233                                 | 4 14+           | 2 172 175   |             |
|                     | 7 111 124         | 2 142 157       | + 241 247                  | 1 182 174     | 2 134 145     | 4 294 313     | 5 245 281   | 4 307 320                                 | 5 0 1+          | 3 195 176   |             |
| 4 4 24              | 1 2 15 25         | 3 177 207       |                            | 2 276 244     | 3 134 110     | 5 +1+ +25     | + 223 235   |   | • 0 ••          | 4 271 275   |             |
|                     |                   |                 | A 134 334                  |               |               |               | 7 347 347   | 0 476 410                                 | 8.1.8 4.21      | 174         |             |



Fig. 1. Molecular structure illustrating thermal ellipsoids and numbering system.

## Table 5. Nonbonding distances

| (i) Intramolecular                    | distances (Å) |                |               |
|---------------------------------------|---------------|----------------|---------------|
| O(1) - O(2)                           | 2.493         | O(2)—C(3)      | 2.990         |
| O(1) - N(1)                           | 2.467         | O(2) - C(6)    | 2.995         |
| O(1) - C(5)                           | 2.563         | O(2)—H(5)      | 2.917         |
| O(1) - N(4)                           | 2.979         | O(2)—H(3)      | 2.733         |
| O(1) - C(1)                           | 2.938         | N(1) - C(5)    | <b>2</b> ·690 |
| O(1) - H(2)                           | 2.617         | H(3) - H(6)    | 2.287         |
| O(2) - N(1)                           | <b>2</b> ·468 | H(10) - N(2)   | 2.536         |
| O(2)-C(5)                             | 2.536         |                |               |
| (ii) Intermolecular                   | distances (Å) |                |               |
| O(1) - H(4)(a)                        | 2.624         | H(4) - H(2)(c) | 2.365         |
| O(2) - H(3)(b)                        | 2.768         | H(3) - H(6)(b) | 2.615         |
| N(3) - N(4)(c)                        | 2.866         | H(6) - H(7)(b) | <b>2·</b> 647 |
| C(9) - H(6) (d)                       | 2.707         |                |               |
| Symmetry operato                      | rs            |                |               |
| · · · · · · · · · · · · · · · · · · · |               | (.) 1.1        | . 1           |

| (a)        | $\frac{1}{2} + x$ , | $\frac{3}{2} - y$ , 1 | -z | ( <i>c</i> ) | $-\frac{1}{2}+x, \frac{1}{2}-y,$    | 1 - z |
|------------|---------------------|-----------------------|----|--------------|-------------------------------------|-------|
| <i>(b)</i> | $\frac{1}{2} - x$   | $-\frac{1}{2}+v$ ,    | Ζ  | (d)          | $\frac{1}{2} - x, \frac{1}{2} + y,$ | Ζ     |

ences therein). The distances and angles around the sulfur atom are similar to those observed in the sulfathiazole polymorphs (Kruger & Gafner, 1972) 1972) when allowances are made for the different types of nitrogen atoms (>N-vs. >N) and the internal compensation in the S-C bond. The S-C(5) and S-N(1) distances are shorter than expected for S-Csp<sup>2</sup> and S-Nsp<sup>2</sup> 'single' bonds [see Ammon, Watts & Stewart (1970) for a listing of S-C bonds]. These data are consistent with some (possibly appreciable) delocalization of the imidazole  $\pi$  systems with the SO<sub>2</sub> group. Some of the angular distortion [N(1)-S-C(5) is  $104.7 (2)^{\circ}$ , O(1)-S-O(2) is 123.2 (2)°] may result from this interaction, but it is difficult to separate this from steric effects. The C-H distances are normal for an X-ray determination as are the benzene C-C distances. The C(2)–C(7) distance of 1.457 (7) is short for a  $Csp^2$ – $Csp^2$ distance; this along with the planarity of the adjacent rings is consistent with some delocalization of the two ring systems.

The interatomic angles in the N(3), N(4)-imidazole are consistent with the N(3)-H tautomeric form established by the electron density maps. In particular the larger internal angle subtended at N(3) compared to N(4) is typical for the protonatde N site (Singh, 1965; Sletten, Sletten & Jensen, 1968). The same tautomer was observed in the histamine imidazole ring in 6histaminopurine (Thewalt & Bugg, 1972).

The data for the least-square planes through the different ring systems are given in Table 7. Each of the individual rings is planar to 0.01 Å while the combined phenylimidazole ring is planar to 0.09 Å. The angle between the two imidazole rings is 100.2° (79.8° between normals, Table 7) and the angle between the imidazole and attached phenyl ring is 7.2° (planes II and IV).

The thermal motion appears to be normal for the geometries involved. The root-mean-square amplitudes of vibration vary from 0.164 to 0.365 Å. The most anisotropic atom is O(1) (0.164–0.285 Å).

### Packing and hydrogen bonding

The most important features of the crystal packing are hydrogen bonding and base stacking. Both of these features are commonly found in nucleic acid constituents and polynucleotides both in the solid and solution states (Ts'o, 1968). Numerous examples of base stacking with purine and pyrimidine bases can be found in the literature (Thewalt & Bugg, 1972; Bugg, Thomas, Sundaralingam & Rao, 1971, and references therein). While the N(3), N(4)-imidazole is involved in hydrogen bonding and base stacking, the N(1), N(2)imidazole and phenyl ring are involved in the conventional herringbone packing of planar aromatic rings.

The molecules form chains in one dimension by  $N-H\cdots N$  hydrogen bonds characterized by



These chains are stacked in the second dimension with 3.41 Å between parallel molecules. The hydrogen bonding and base stacking are shown in Fig. 4; the top view is normal to the plane of the hydrogen bonded imidazole ring. The overlap is partial but specific in the sense that N(3) and C(5) of each imidazole overlap above and below with C(5) and N(3), respectively, of stacked imidazoles. The orientation of



Fig. 2. Bond distances (Å).



Fig. 3. Bond angles (°).

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Table 6. Comparison of imidazole distances

|  | intrate          |
|--|------------------|
| $\Omega(5)$ N(4) 1.272 (() 1.2 |                  |
| C(5) = N(4) 1.377 (6) 1.396 (6) 1.378 (5) 1.372 (8) 1.366 (8) 1.374 (8)  | 1.3/2(7)         |
| N(4)-C(4) 1·319 (6) 1·298 (7) 1·326 (5) 1·345 (7) 1·326 (8) 1·312 (8)  | 1.316 (7)        |
| C(4)-N(3) 1.353 (6) 1.366 (6) 1.349 (5) 1.344 (8) 1.318 (8) 1.330 (8)  | 1.329 (7)        |
| N(3)-C(6) 1·361 (6) 1·390 (6) 1·369 (5) 1·385 (7) 1·366 (8) 1·374 (8)  | 1.352 (7)        |
| C(6)-C(5) 1·362 (6) 1·345 (7) 1·358 (5) 1·362 (9) 1·340 (8) 1·403 (8)  | 1.366 (7)        |
| Reference Present work Martínez- Beard & Thewalt & Watson, Swee  | et Santoro,      |
| Carrera Lenhert (1968) Bugg (1972) & Marsh   | Mighell, Zocchi  |
| (1966) (1965)  | & Reimann (1969) |

\* The histamine imidazole ring used.

(

the hydrogen bonding and base stacking were established explicitly by fixing an orthogonal coordinate system to the imidazole ring and determining its orientation relative to the cell edges. Two vectors originating from the midpoint of N(3) and N(4) were used to establish the local coordinate system, **u** in the direction of the midpoint to N(3) and **v** in the direction of the midpoint to C(4). The three local axes were taken according to

$$\mathbf{m} = \mathbf{u}$$
$$\mathbf{m} = (\mathbf{u} \times \mathbf{v}) \times \mathbf{u}$$
$$\mathbf{s} = \mathbf{u} \times \mathbf{v}$$



Fig. 4. Front and top views of the base stacking and hydrogen bonding in 1-(4-imidazolylsulfonyl)-4-phenylimidazole (R represents the phenylimidazole group).

### Table 7. Least-squares planes through rings

- (a) Equations of planes in Cartesian coordinates relative to a, b, c.
  - I 0.0055X + 0.9277Y 0.3732Z + 9.993 = 0
  - II -0.5022X + 0.4774Y + 0.7211Z 9.897 = 0
  - III -0.4457X + 0.5317Y + 0.7202Z 1.057 = 0
  - IV 0.4106X + 0.5620Y + 0.7180Z 1.101 = 0
- (b) Deviations (Å) from the planes (asterisks mark atoms included in the plane calculation)

|           | Ι             | II      | III              | IV      |
|-----------|---------------|---------|------------------|---------|
| S         | -0.066        | 0.150   | -0.034           | -0.213  |
| O(1)      | -0.853        | -0.271  | -0.423           | -0.582  |
| O(2)      | -0.314        | -0.452  | -0.716           | -0.941  |
| N(3)      | -0.006*       |         |                  |         |
| N(4)      | -0.008*       |         |                  |         |
| C(4)      | 0.009*        |         |                  |         |
| C(5)      | 0.005*        |         |                  |         |
| C(6)      | 0.000*        |         |                  |         |
| H(1)      | -0.104        |         |                  |         |
| N(1)      |               | -0.010* | -0.086*          | -0.202  |
| N(2)      |               | 0.000*  | 0.091*           | 0.074   |
| C(1)      |               | 0.006*  | 0.032*           | -0.023  |
| C(2)      |               | -0.007* | 0.024*           | -0.030  |
| C(3)      |               | 0.010*  | -0.061*          | -0.175  |
| C(7)      |               | -0.065  | 0·014*           | -0.012* |
| C(8)      |               | 0.055   | 0.071*           | 0.007*  |
| C(9)      |               | -0·016  | 0.044*           | 0.006*  |
| C(10)     |               | -0.207  | -0.040*          | -0.014* |
| C(11)     |               | -0.584  | <i>-</i> −0·055* | 0.009*  |
| C(12)     |               | -0.220  | -0.034*          | 0.004*  |
| c) Dihedr | al angles (°) |         |                  |         |
| IS 0(1)   | 0(2)          |         |                  |         |
| IS N(1)   | C(5)          | 80.1    | II_III           | 1.5     |
| 10, M(I)  | , (),<br>-H   | 79.8    |                  | 7.2     |
| I-        |               | 76.9    |                  | 2.7     |
| I-<br>I-  | -IV           | 75.2    | 111-1 4          | 41      |
| 1         | <b>-</b> 7    | 124     |                  |         |

Then **h** is the direction of the hydrogen-bonded chains, **s** is the stacking direction (imidazole plane normal) and **m** completes the orthogonal coordinate system. The matrix of angles describing the orientation of the local coordinate system and the cell edges is

|          | a      | b     | с      |
|----------|--------|-------|--------|
| h        | 179·0° | 89·9° | 90∙0°  |
| m        | 87•4   | 66.9  | 23.3   |
| <b>S</b> | 90.3   | 23.1  | 113.1. |

Thus the hydrogen-bond direction  $\mathbf{h}$  is parallel to  $\mathbf{a}$  and the stacking direction  $\mathbf{s}$  is normal to  $\mathbf{a}$ , but in a general orientation with respect to  $\mathbf{b}$  and  $\mathbf{c}$ .

. . .. . .

Other examples of base stacking of simple imidazoles are imidazolium dihydrogen orthophosphate (Blessing & McGandy, 1972) and 1,3-dimethyl-2(3H)-imidazolethione (Ansell, Forkey & Moore, 1970) for which stacking views are provided by the authors. Stacking views for imidazole (Martínez-Carrera, 1966) and 1,3diphosphorylimidazole (Beard & Lenhert, 1968) were drawn and are shown in Fig 5. The overall hydrogen bonding and base stacking appear to be more extensive in 1-(4-imidazolylsulfonyl)-4-phenylimidazole than in other simple imidazoles, but the number of available structures is too small to make any generalizations. It is noteworthy, however, that the stacking pattern found here is consistent with the idea that dipoleinduced dipole forces (Bugg et al., 1971, and references therein) are responsible for solid-state base stacking in purine and pyrimidine bases.

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Fig. 5. Front and top views of the stacking in: (a) imidazole (Martínez-Carrera, 1966), (b) 1,3-diphosphorylimidazole (Beard & Lenhert, 1968).

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# The Molecular and Crystal Structure of the Sodium Salt of Deoxyadenosine-5'-phosphate Hexahydrate

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The crystal structure of the sodium salt of deoxyadenosine-5'-phosphate hexahydrate has been determined by X-ray diffraction techniques. The unit cell is orthorhombic, space group  $P2_12_12_1$ , with cell dimensions a = 43.64 (2), b = 6.908 (4), c = 6.826 (4) Å and Z = 4. The data (1806 reflexions) were collected photographically by equi-inclination Weissenberg geometry and estimated visually. The structure was solved by the symbolic addition procedure and refined to an R value of 0.060. 24 out of 25 hydrogen atoms were located. The sugar ring has the conformation C(2')-endo, C(3')-endo and the glycosidic torsional angle ( $\chi_{CN}$ ) is 63.4°. The sugar ring oxygen O(1') seems to participate in a hydrogen bond with the amino nitrogen of the base, a feature hitherto not clearly shown in similar structures. The stacking of adenine bases at 3.45 Å with considerable overlap is another interesting feature. The sodium ion has a nearly octahedral coordination with water oxygen atoms at distances of 2.374 to 2.454 Å. The crystal structure may be viewed as consisting of alternate channels of water molecules (sodium ion polyhedra) and nucleotides.

### Introduction

Recently, Jacob and colleagues at our Institute have prepared many nucleic acid reactive antibodies for immunological studies, specific to deoxyribonucleotide antigens and in particular to deoxyadenosine-5'-monophosphate (5'-dAMP) (Humayun & Jacob, 1973). This paper reports the complete molecular and crystal structure of this nucleotide.\* The present analysis continues our earlier studies on the conformations of DNA constituents (Viswamitra, Reddy, Lin & Sundaralingam, 1971).

### Experimental

# Crystal growth and crystal data

The material used in the present work was obtained from Sigma Chemical Company (U.S.A.) as a disodium salt of 2'-deoxyadenosine-5'-monophosphoric acid. It

A C 31B – 2\*

was crystallized by slow diffusion of dioxane into water solutions of the sample. The crystal data were obtained from rotation, Weissenberg and precession photographs using Cu Ka radiation (Table 1). The density measured by the flotation method using a mixture of carbon tetrachloride and acetone is 1.53 g cm<sup>-3</sup>, suggesting a chemical formula of the molecule in the asymmetric unit as  $C_{10}H_{13}N_5Na_2O_6P.5H_2O$  ( $d_{calc} =$ 1.511 g cm<sup>-3</sup>). However, detailed structure analysis showed that the molecule exists as

 $C_{10}H_{13}N_5NaO_6P.6H_2O$ , in the crystal. The crystal data are presented in Table 1 and the numbering scheme for the molecule is shown in Fig. 1.

# Intensity data

The intensity data were collected with Cu  $K\alpha$  radiation from a crystal of size  $0.5 \times 0.4 \times 0.25$  mm, by the equi-inclination Weissenberg technique for layers hk0hk6 and h0l. In all, 1806 reflexions were estimated visually by using a calibrated film strip prepared with the experimental crystal. The data were corrected for

<sup>\*</sup> A preliminary communication on this structure has already appeared (Reddy & Viswamitra, 1973).