CO(II)   2,2'-DICARBOXYDIPHENYLDISULFIDE   CO(II)   2,2'-DICARBOXYDIPHENYLDISULFIDE

Fig. 3. A stereo view of the packing within the unit cell using ellipsoids of 15% probability. Three-atom 'molecules' are methanol oxygen atoms with two disordered half-carbon atoms. Two-atom molecules are methanol, and a water molecule is represented by only its oxygen atom. The view is nearly along c, with b horizontal and a vertical in the plane of the page.

etry of the disulfide linkage. The C(11)–S(5)–S(6)–C(18) dihedral angle is 86·7° and the S(5)–S(6) bond is 2·047 (3) Å. These values can be compared to those of 90·5° and 2·060 (3) Å found in an analogous compound, 2,2'-diaminodiphenyl disulfide (Lee & Bryant, 1970), (to illustrate the similarity, the present anion may be named hydrogen-2,2'-dicarboxylate diphenyl disulfide), as well as to many other organic disulfides (Hordvik, 1966; Lee, 1972). A stereo view of the packing is shown in Fig. 3.

References

BOSCHI, T., CROCIANI, B., TONIOLO, L. & BELLUCO, U. (1970). Inorg. Chem. 9, 532–537.

CHALLENGER, F. (1959). Aspects of the Organic Chemistry of Sulphur. London: Butterworths.

DOYLE, P. A. & TURNER, P. S. (1968). Acta Cryst. A24, 390–397.

HEMMERICH, P. (1966). The Biochemistry of Copper, edited by PEISACH, AISEN & BLUMBERG, pp. 15–34. New York: Academic Press.

HORDVIK, A. (1966). Acta Chem. Scand. 20, 1885–1891.

HUBBARD, C. R., QUICKSALL, C. O. & JACOBSON, R. A. (1971). ALFF, Ames Laboratory Fast Fourier, Iowa State Univ., U.S.A.

KAWANISHI, S., YOKOYAMA, A. & TANAKA, H. (1972). Chem. Pharm. Bull. 20, 262–268.

JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

LEE, J. D. (1972). Naturwissenschaften, 59, 36–37.

LEE, J. D. & BRYANT, M. W. R. (1970). Acta Cryst. B26, 1729–1735.

OTTERSEN, T., WARNER, L. G. & SEFF, K. (1973). Chem. Commun. 876–877.

ZALKIN, A., RUBEN, H. & TEMPLETON, D. H. (1962). Acta Cryst. 15, 1219–1223.

The 2:1 Crystal Complex of 5,5-Diethylbarbituric Acid (Barbital) and Caffeine

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Triclinic, $P\bar{1}$; $a = 14\cdot627$ (4), $b = 14\cdot160$ (4), $c = 6\cdot902$ (2) Å, $\alpha = 92\cdot25$ (4), $\beta = 92\cdot80$ (4), $\gamma = 100\cdot75$ (4)°; $Z = 2$ for $2C_8H_{12}N_2O_3.C_8H_{10}N_4O_2$; $D_{meas} = 1\cdot344$ g cm^{-3}, $D_x = 1\cdot334$ g cm^{-3}; m.p. 142°C; $\mu(Cu\ K\alpha) = 8\cdot67$ cm^{-1}. The crystal structure was determined by direct methods from 4665 intensity data which were measured with a computer-controlled four-circle diffractometer and nickel-filtered Cu $K\alpha$ radiation. Refinement by a block-diagonal least-squares procedure gave a final R index of 0·053. Bond lengths and angles are similar to those observed in related crystal structures.

Introduction

The crystals were prepared as described by Higuchi & Lach (1954). Integrated intensity data were col-

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lected from a crystal elongated along c and exhibiting the forms {100}, {010}, and {001}. The crystal was mounted with the c* reciprocal axis along the diffractometer φ axis. 4665 independent reflections in the range sin θ/λ ≤ 0·59 Å^{-1} were scanned in the θ–2θ mode at a rate of 2° min^{-1}. A variable 2θ scan width was used, based on a minimum of 1·5°. Stationary
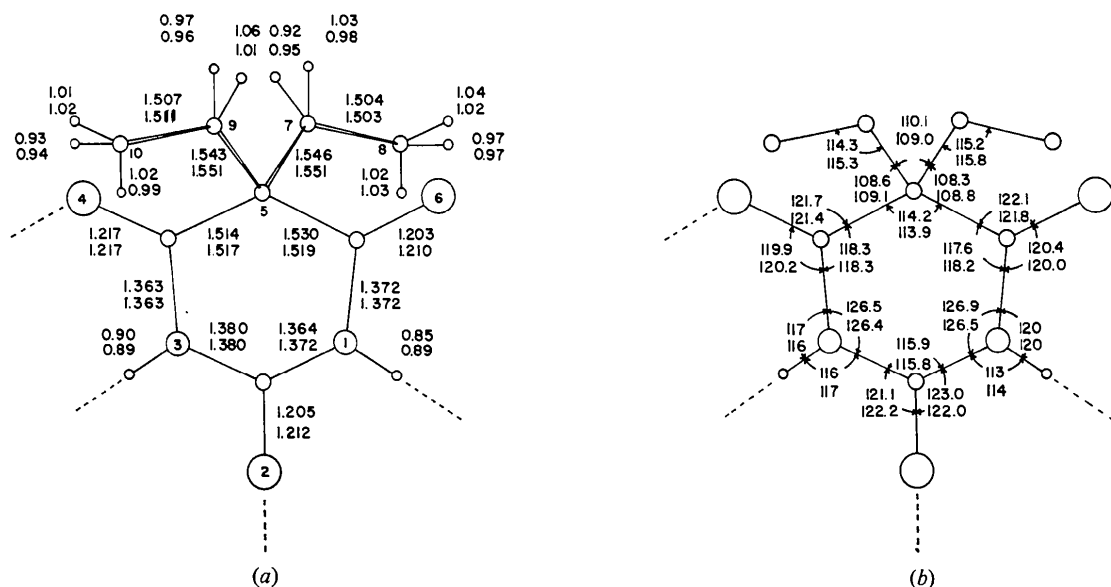
Fig. 1. Bond lengths (a) and angles (b) for the barbital molecules. Circles of decreasing radius represent oxygen, nitrogen, carbon and hydrogen atoms. For each parameter, the values given are for molecule A (above) and molecule B (below). Estimated standard deviations in distances are: 0·006 Å for ring and carbonyl bonds, 0·007 Å for C(5)–C(α) bonds of the ethyl groups, 0·008 Å for the C(α)–C(β) bonds, 0·05 Å for N–H bonds, and 0·06 Å for C–H bonds. The estimated error in a bond angle determination is 0·4°. Dashed lines indicate atoms involved in hydrogen bonding.

Table 1. *Atomic parameters*

Positional parameters are given as fractions of the lattice translations. Anisotropic temperature factors correspond to the expression: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$, and isotropic temperature factors to the expression: $\exp(-B\sin^2\theta/\lambda^2)$. The entry U_k is the r.m.s. atomic vibrational amplitude (Å) in the direction of the kth principal axis of the thermal ellipsoid. These were calculated from the experimental β_{ij} values. For barbital parameters, the values given are for molecule A (above) and molecule B (below). E.s.d.'s shown in parentheses refer to the least significant figures in parameter values.

(a) Carbon, nitrogen and oxygen atoms

(All parameters × 10^4, except $\beta_{33} \times 10^3$ and $U_k \times 10^2$)

(i) Barbital	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	U_1	U_2	U_3
N(1)	2054 (3)	2105 (2)	7951 (6)	43 (2)	30 (2)	27 (1)	6 (2)	21 (4)	33 (3)	16	21	26
	2618 (2)	5810 (2)	7305 (5)	23 (2)	37 (2)	24 (1)	5 (1)	−2 (3)	25 (3)	15	18	25
C(2)	1185 (3)	1928 (3)	8635 (7)	42 (2)	38 (2)	22 (1)	11 (2)	14 (4)	22 (4)	18	21	24
	2958 (3)	5039 (3)	7918 (6)	31 (2)	35 (2)	20 (1)	6 (2)	15 (4)	19 (4)	18	18	22
O(2)	723 (3)	2544 (2)	8903 (6)	60 (2)	46 (2)	40 (1)	24 (2)	45 (4)	47 (4)	18	24	32
	2477 (2)	4238 (2)	7837 (5)	43 (2)	34 (2)	33 (1)	0 (1)	−3 (3)	21 (3)	17	22	28
N(3)	861 (2)	993 (2)	9043 (6)	36 (2)	33 (2)	25 (1)	6 (1)	30 (3)	19 (3)	17	18	25
	3883 (2)	5231 (2)	8602 (5)	28 (2)	33 (2)	24 (1)	9 (1)	3 (3)	29 (3)	16	18	24
C(4)	1330 (3)	246 (3)	8868 (6)	37 (2)	32 (2)	20 (1)	4 (2)	9 (4)	9 (4)	18	20	22
	4466 (3)	6111 (3)	8810 (6)	26 (2)	38 (2)	21 (1)	8 (2)	12 (3)	21 (4)	16	19	23
O(4)	994 (2)	−527 (2)	9423 (5)	50 (2)	34 (2)	28 (1)	4 (1)	33 (3)	22 (3)	17	22	27
	5241 (2)	6208 (2)	9619 (5)	30 (1)	51 (2)	28 (1)	8 (1)	−10 (3)	33 (3)	17	21	27
C(5)	2251 (3)	399 (3)	7919 (7)	37 (2)	33 (2)	24 (1)	7 (2)	23 (4)	20 (4)	18	19	24
	4139 (3)	6944 (3)	7929 (7)	26 (2)	32 (2)	25 (1)	4 (2)	1 (4)	21 (4)	17	17	25
C(6)	2594 (3)	1437 (3)	7451 (7)	38 (2)	40 (2)	27 (1)	5 (2)	19 (4)	28 (4)	18	21	26
	3119 (3)	6720 (3)	7180 (7)	27 (2)	38 (2)	27 (1)	6 (2)	5 (4)	30 (4)	17	18	26
O(6)	3317 (3)	1674 (3)	6708 (7)	51 (2)	58 (2)	49 (1)	8 (2)	77 (4)	58 (4)	18	24	36
	2748 (2)	7320 (2)	6489 (6)	37 (2)	51 (2)	51 (1)	10 (1)	−19 (4)	76 (4)	17	21	37
C(7)	2131 (4)	−275 (3)	5994 (7)	55 (3)	45 (3)	26 (1)	11 (2)	42 (5)	12 (4)	20	21	27
	4748 (3)	7194 (3)	6200 (7)	32 (2)	44 (2)	25 (1)	2 (2)	4 (4)	36 (4)	17	20	26
C(8)	1328 (4)	−188 (4)	4617 (8)	80 (4)	67 (4)	23 (1)	5 (3)	8 (6)	14 (5)	23	25	30
	4764 (3)	6371 (4)	4669 (7)	45 (3)	65 (3)	23 (1)	8 (2)	5 (4)	13 (5)	22	23	25
C(9)	3000 (4)	139 (4)	9317 (9)	43 (3)	57 (3)	37 (2)	10 (2)	0 (5)	52 (6)	20	22	31
	4298 (3)	7832 (3)	9482 (8)	38 (2)	38 (2)	30 (1)	6 (2)	11 (4)	14 (4)	19	20	27
C(10)	3195 (4)	779 (5)	11216 (9)	54 (3)	111 (5)	31 (2)	−7 (3)	−17 (6)	47 (7)	22	26	36
	3636 (4)	7765 (4)	11101 (9)	67 (3)	57 (3)	32 (2)	19 (3)	35 (6)	22 (5)	22	25	29

Table 1 (cont.)

(ii) Caffeine

N(1)	1972 (2)	3786 (3)	2937 (5)	28 (2)	53 (2)	22 (1)	15 (2)	4 (3)	10 (4)	16	23	23
C(1)	2890 (3)	3500 (4)	3000 (9)	32 (2)	82 (4)	36 (2)	28 (2)	13 (5)	22 (6)	15	29	29
C(2)	1216 (3)	3071 (3)	3253 (7)	40 (2)	49 (3)	21 (1)	16 (2)	5 (4)	12 (4)	18	22	23
O(2)	1312 (3)	2260 (3)	3534 (6)	57 (2)	56 (2)	39 (1)	27 (2)	14 (4)	42 (4)	19	26	31
N(3)	352 (2)	3327 (2)	3247 (5)	31 (2)	35 (2)	21 (1)	7 (1)	7 (3)	9 (3)	18	19	22
C(3)	−461 (3)	2590 (3)	3512 (8)	40 (2)	37 (2)	31 (1)	4 (2)	19 (4)	18 (4)	18	21	27
C(4)	267 (3)	4238 (3)	2849 (6)	27 (2)	37 (2)	15 (1)	7 (2)	3 (3)	2 (3)	17	18	20
C(5)	1022 (3)	4911 (3)	2499 (6)	29 (2)	40 (2)	17 (1)	8 (2)	5 (3)	2 (3)	17	19	21
C(6)	1946 (3)	4731 (3)	2510 (6)	28 (2)	52 (2)	17 (1)	5 (2)	5 (3)	−5 (4)	17	19	24
O(6)	2653 (2)	5298 (3)	2213 (5)	30 (2)	64 (2)	33 (1)	1 (1)	15 (3)	8 (4)	17	26	28
N(7)	675 (2)	5731 (2)	2186 (5)	29 (2)	36 (2)	18 (1)	4 (1)	6 (3)	9 (3)	17	19	21
C(7)	1215 (3)	6654 (3)	1730 (7)	41 (2)	40 (2)	26 (1)	0 (2)	18 (4)	13 (4)	18	22	25
C(8)	−247 (3)	5504 (3)	2341 (6)	31 (2)	40 (2)	18 (1)	8 (2)	2 (3)	6 (4)	18	20	21
N(9)	−534 (2)	4596 (2)	2763 (5)	26 (2)	36 (2)	18 (1)	7 (1)	4 (3)	4 (3)	16	19	21

Table 1 (cont.)

(b) Hydrogen atoms

Positional parameters × 10³

(i) Barbital

	x	y	z	B (Å²)
H(1)	223 (4)	269 (4)	771 (8)	6 (1)
	200 (3)	569 (4)	705 (7)	5 (1)
H(3)	30 (3)	88 (4)	954 (7)	5 (1)
	410 (3)	475 (3)	911 (7)	4 (1)
H(71)	205 (3)	−89 (4)	639 (7)	4 (1)
	535 (3)	748 (4)	681 (7)	4 (1)
H(72)	276 (4)	−12 (4)	535 (7)	5 (1)
	451 (3)	771 (4)	563 (7)	4 (1)
H(81)	69 (4)	−40 (4)	521 (8)	6 (1)
	502 (4)	582 (4)	524 (7)	5 (1)
H(82)	140 (4)	48 (4)	432 (9)	7 (1)
	415 (4)	605 (4)	411 (7)	5 (1)
H(83)	131 (5)	−64 (5)	336 (9)	8 (2)
	514 (4)	656 (4)	350 (8)	6 (1)
H(91)	282 (4)	−53 (4)	961 (8)	6 (1)
	493 (4)	790 (4)	998 (7)	5 (1)
H(92)	363 (4)	20 (4)	858 (9)	6 (1)
	423 (4)	841 (4)	876 (7)	5 (1)
H(101)	264 (5)	74 (5)	1184 (9)	9 (2)
	361 (4)	719 (4)	1167 (9)	7 (1)
H(102)	345 (5)	145 (5)	1086 (9)	8 (2)
	300 (4)	780 (4)	1060 (9)	6 (1)
H(103)	367 (5)	55 (5)	1208 (9)	8 (2)
	383 (4)	833 (4)	1214 (9)	7 (1)

(ii) Caffeine

	x	y	z	B (Å²)
H(11)	338 (5)	409 (5)	340 (10)	9 (2)
H(12)	297 (5)	327 (5)	173 (10)	9 (2)
H(13)	297 (5)	311 (5)	414 (11)	9 (2)
H(31)	−101 (4)	287 (4)	374 (7)	5 (1)
H(32)	−56 (4)	207 (5)	247 (9)	8 (2)
H(33)	−34 (4)	227 (4)	471 (9)	7 (1)
H(71)	80 (4)	709 (4)	159 (8)	6 (1)
H(72)	152 (4)	654 (4)	52 (9)	7 (1)
H(73)	167 (4)	692 (4)	281 (8)	5 (1)
H(8)	−65 (3)	596 (3)	217 (7)	4 (1)

background counts of 20 s were recorded at each of the 2θ scan limits. There were 882 reflections for which the integrated intensity I was less than $1 \cdot 2 \ \sigma(I)$. They were assigned intensities of $\sigma(I)/2$, where $\sigma(I)$ is the standard deviation of I as estimated from counting statistics. No corrections were made for X-ray absorption or extinction.

The structure was solved by direct methods with the symbolic addition procedure followed by automated tangent refinement (Karle & Karle, 1966). All 40 non-hydrogen atoms were found in the first E map, and all 34 hydrogen atoms were subsequently found in a difference Fourier synthesis.

The positional and anisotropic thermal parameters for heavier atoms and positional and isotropic thermal parameters for hydrogen atoms were refined by a block-diagonal least-squares procedure. The atomic form factors used were those of Cromer & Waber (1965) for carbon, nitrogen and oxygen, and Stewart, Davidson & Simpson (1965) for hydrogen. The function minimized was $\sum w_H \Delta_H^2$, where $\Delta_H = |F_H^{\mathrm{obs}}| - |F_H^{\mathrm{calc}}|$ and $w_H^{-1} = 1 \cdot 2 + |0 \cdot 05 F_H|^2$. Convergence occurred with R (all reflections) $= \sum|\Delta_H|/\sum|F_H^{\mathrm{obs}}| = 0 \cdot 053$. The atomic parameters and their e.s.d.'s are in Table 1.*

Discussion

The present discussion is restricted to the molecular structures of the components, because the intermolecular aspects of the crystal structure, including the hydrogen bonding, ring stacking and carbonyl–carbonyl interactions, have been described elsewhere (Craven & Gartland, 1970).

(a) Barbital

Bond lengths and angles for the two crystallographically independent molecules of barbital are shown in Fig. 1(a) and (b). These have not been corrected for thermal motion effects. There are no significant differences between the values determined for the two different molecules. In addition, the values are in good agreement with those found in polymorphs of barbital itself (Craven, Vizzini & Rodrigues, 1969).

Both molecules A and B exhibit small differences (0·01 Å) in the lengths of pairs of C–N and C=O bonds,

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e.g. C(6)N(1) and C(4)N(3) which should be equivalent in an isolated molecule. These differences are not significant in terms of their e.s.d.'s. However, Craven, Cusatis, Gartland & Vizzini (1973) have pointed out that these differences occur with the same sense in a number of barbiturate crystal structures, and that they seem to arise whenever atom O(4) is hydrogen bonded, but O(6) is not. The slight puckering of the oxopyrimidine ring in molecules *A* and *B* is similar to that observed in other barbiturate crystal structures [see Fig. 3 in Craven *et al.* (1973)].

In both molecules *A* and *B*, the hydrocarbon chains consisting of the ethyl groups and C(5) are distorted from idealized all-*trans* conformations by small twists about C(5)–C(α) bonds. In molecule *B* the distortions are slightly larger. Torsion angles about the C(5)–C(α) bonds are 182·4 and 182·5° for molecule *A* and 183·6 and 186·5° for molecule *B*. When viewed along the C(5)$\cdots$C(2) direction, the hydrocarbon backbone for each molecule assumes a slight 'S' shape such that the terminal atom C(8) lies closer to O(4) than to O(6) and *vice versa* for the terminal atom C(10).

(b) Caffeine

Bond lengths and angles for caffeine in the 2:1 barbital–caffeine complex are shown in Fig. 2(*a*) and (*b*). Differences between the caffeine molecular dimensions determined in this complex and those found in a 1:1 complex with 5-chlorosalicylic acid (Shefter, 1968) are also shown in Fig. 2. There is overall agreement between the two sets of parameters. The only possibly significant differences are in the bond length C(6)–O(6) ($\Delta = 2 \cdot 6\sigma$), and the bond angle C(5)–N(7)–C(7) ($\Delta = 3 \cdot 2\sigma$). The smaller C(5)–N(7)–C(7) angle in the complex with barbital may be attributed to a repulsion between the caffeine methyl group C(7) and the barbital oxygen atom O(2) of molecule *A* (Craven & Gartland, 1970).

Although the atoms of the purine ring system are almost coplanar, there are small but significant displacements of the methyl carbon atoms (0·06, 0·02 and 0·01 Å) and the carbonyl O(2) atom (0·06 Å) from this plane (Fig. 3). A similar pattern of atomic displacements is reported for the caffeine molecule in the complex with 5-chlorosalicylic acid (Shefter, 1968). However, in this case, there is also a slight folding of the molecule about the C(4)–C(5) bond. The orientation of the methyl hydrogen atoms is similar in both crystal complexes for the methyl substituents at the nitrogen atoms N(1) and N(7). In the complex with 5-chlorosalicylic acid, the methyl group at N(3) is twisted about 40° around the N(3)–C bond relative to the configuration shown in Fig. 3. Presumably these differences are the result of crystal packing effects.
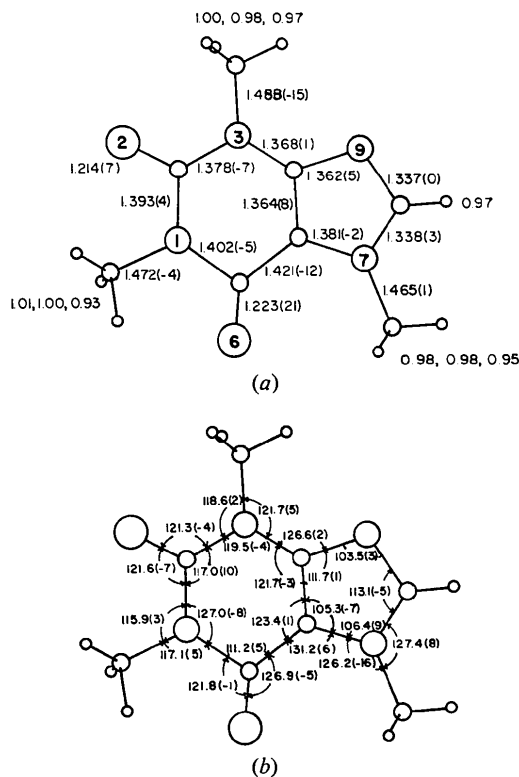
Fig. 2. Bond lengths (*a*) and angles (*b*) for caffeine. The values shown are for the 2:1 complex of barbital with caffeine. The quantities in parentheses are differences between the presently reported values and those found in a 1:1 complex of caffeine with 5-chlorosalicyclic acid (Shefter, 1968). Thus a negative number indicates that the larger parameter was found in the latter complex. Estimated standard errors in distances are 0·06 Å for bonds involving hydrogen; otherwise, 0·006 Å. The estimated error in an angle is 0·4°.
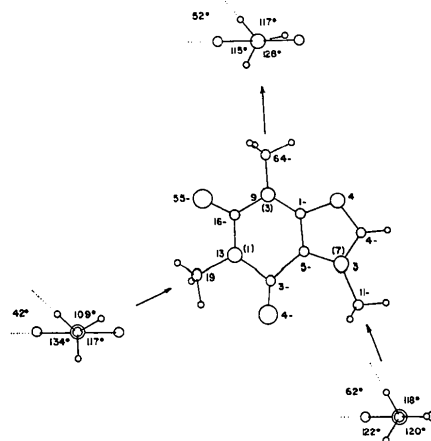

Fig. 3. Geometry of the caffeine molecule. Nitrogen atoms which have methyl substituents are numbered in parentheses. For each non-hydrogen atom, the distance (Å × 10³) above or below the best least-squares plane through the purine atoms is indicated. The orientations of methyl hydrogen atoms are shown in projections down appropriate N–C bonds.

References

CRAVEN, B. M., CUSATIS, C., GARTLAND, G. L. & VIZZINI, E. A. (1973). *J. Mol. Struct.* **16**, 331–342.

CRAVEN, B. M. & GARTLAND, G. L. (1970). *J. Pharm. Sci.* **59**, 1666–1670.

CRAVEN, B. M., VIZZINI, E. A. & RODRIGUES, M. M. (1969). *Acta Cryst.* **B25**, 1978–1993.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

HIGUCHI, T. & LACH, J. L. (1954). *J. Amer. Pharm. Assoc. Sci. Ed.* **43**, 349–354.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.

SHEFTER, E. (1968). *J. Pharm. Sci.* **57**, 1163–1168.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

The Geometry of Polyhedral Distortions. Predictive Relationships for the Phosphate Group

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The shapes of 211 phosphate tetrahedra have been studied. Their dimensions are known precisely from published X-ray and neutron-diffraction investigations. Results: (1) The site symmetry of the P atoms is found in 85% of the cases to be 1. Other observed symmetries are m, 2, 3, $\bar{4}$, mm, $\bar{4}2m$, 222 and 23. (2) The deviations from regular symmetry, $\bar{4}3m$, are pronounced. The distortions can be measured by defining for every phosphate group three distortion indices: $DI(TO) = (\sum |TO_i - TO_m|)/4TO_m$, $DI(OTO) = (\sum |OTO_i - OTO_m|)/6OTO_m$ and $DI(OO) = (\sum |OO_i - OO_m|)/6OO_m$, where TO is the distance P–O, OTO the angle O–P–O, OO the distance O–O, the subscripts m refer to the mean and i to individual values. The average distortion indices for all groups are: $DI(TO) = 0.021$, $DI(OTO) = 0.028$, $DI(OO) = 0.012$. This means that distortions are more pronounced in the P–O distances than in O–O and thus the phosphate group can be viewed, to a first approximation, as a rigid regular arrangement of O atoms, with the P atoms displaced from their centroid. (3) *Mean* P–O distances of the phosphate groups vary from 1·506 to 1·572 Å. (4) *Individual* P–O distances are correlated with the bond strengths received by the individual oxygen atoms. (5) The individual O–P–O angles are strongly correlated with the average of the P–O distances on the sides of the angle, and with the opposite O–O distance. The various correlations are strong enough to formulate six equations which are useful for predictive purposes: the mean P–O distances can be calculated from the coordination numbers and the distortion indices; the individual P–O distances follow from the bond strength distribution; the bond angles are based on the normalized bond lengths; the mean O–O distances are a function of the mean P–O distances and the distortion indices; the lengths of shared tetrahedral edges depend on the number of shared edges per tetrahedron. Some of the correlations are affected by the presence of shared edges in the phosphate groups and differ for various subpopulations of the sample (ortho-, di-, ring-, poly-, acid or organic phosphates). The calculated shapes can be used as input to computer simulation of crystal structures.

Introduction

The arrangement of four oxygen atoms around a central pentavalent phosphorus atom is called the tetrahedral phosphate group because the oxygen ligands are distributed over the four corners of a tetrahedron. A regular tetrahedron possesses point group symmetry $\bar{4}3m$ or 23. However, to my knowledge no phosphate tetrahedron observed so far in a crystalline solid is located at a site with $\bar{4}3m$ symmetry. The site symmetries of the phosphate group in Ag_3PO_4 (Helmholz, 1936) and of one of the PO_4^{3-} groups in $Na_6F(OH_2)_{18}$ (NaH_2O) (PO_4)$_2$ (Tillmanns & Baur, in preparation) are 23. However, these data are not used here because in the first case the structure is not determined precisely, while in the second case the phosphate group is disordered and therefore its actual dimensions are not precisely known. The site symmetry of 85% of the

phosphate groups studied in this paper is 1 (Table 1). Most phosphate tetrahedra deviate significantly in their dimensions from the values expected for a regular tetrahedral arrangement. The geometry of these deviations and the extent and the limits of the distortions are the topics of this study. 'Tetrahedron' is used to

Table 1. *Site symmetries of a sample of* 211 *phosphate groups observed in crystalline solids* (*see Appendix*)

Symmetry	Number of groups	% of total
1	179	84·8
m	16	7·6
2	7	3·3
3	4	1·9
$\bar{4}$	2	0·9
mm	1	0·5
222	1	0·5
$\bar{4}2m$	1	0·5