All the calculations were carried out on the FACOM 270-30 at this Institute with a local version of the Universal Crystallographic Computation Program System, UNICS (1967, Crystallographic Society of Japan). Part of the cost of this research was met by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.

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The Crystal Structure of the Triclinic 1:2 Complex of Hexamethylphosphoramide with 5,5-Diethylbarbituric Acid (Barbital)

BY I-NAN HSU* AND B. M. CRAVEN

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, *U.S.A.*

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Hexamethylphosphoramide, $[(CH_3)_2N]_3PO$, (M.W. 179·2) and barbital, $C_8H_{12}N_2O_3$, (M.W. 184·2) form a 1:2 triclinic complex, m.p. 124°C, space group $P\bar{1}$, with $a=6{\cdot}889$ (1), $b=12{\cdot}568$ (1), and $c=17{\cdot}944$ (2) Å, $\alpha=75{\cdot}76$ (1), $\beta=87{\cdot}85$ (1), and $\gamma=76{\cdot}31$ (1)°, $d_{meas}=1{\cdot}246$ g cm^{-3}, $Z=2[(CH_3)_2N]_3+4C_8H_{12}N_2O_3$, and a monoclinic complex of undetermined composition, m.p. 67°C, space group Cc or $C2/c$ with $a=45{\cdot}64$, $b=20{\cdot}29$, and $c=13{\cdot}91$ Å, $\beta=106{\cdot}4$°, $d_{meas}=1{\cdot}172$ g cm^{-3}, $Z=48$ molecules. The crystal structure of the triclinic complex has been determined by the heavy-atom method, from 6020 integrated X-ray intensities measured on a computer-controlled four-circle diffractometer, using graphite-monochromated Cu $K\alpha$ radiation. Refinement by a block-diagonal least-squares procedure gave a final R value of 0·062 for all reflections. The hydrogen bonding is of interest as a model for possible barbiturate–phospholipid interactions. There are two rather strong NH···O=P hydrogen bonds (N···O distances 2·81, 2·84 Å) formed at the phosphoryl oxygen atom. There are also two NH···O=C hydrogen bonds which both form at the same barbital oxygen atom (N···O distances 2·92, 2·93 Å).

Introduction

The drug-active barbiturates, such as 5,5-diethylbarbituric acid or barbital (Fig. 1), form crystal complexes with a variety of molecules which are of biological interest, such as adenine derivatives (Kyogoku, Lord & Rich, 1968; Kim & Rich, 1968; Voet, 1972), amides (Gartland & Craven, 1974; Hsu & Craven, 1974*a*), and imidazole (Hsu & Craven, 1974*b*). The most important molecular interactions in these crystal structures are the hydrogen bonds. Those hydrogen bonds in which the barbiturate NH groups are donors tend to be short, whereas those in which barbiturate oxygen atoms are acceptors tend to be long (Gartland & Craven, 1974; Hsu & Craven, 1974*b*). This suggests that barbiturates are better hydrogen-bonding donors than acceptors and that the preferred barbiturate binding sites in bio-

* Present address: Department of Chemistry, University of Toronto, Ontario, Canada M5S 1A1.

chemical systems are likely to involve a strong hydrogen-bonding acceptor group. The phosphoryl oxygen atoms of phospholipids might satisfy this requirement. Thus, n.m.r. studies in deuterochloroform solution (Novak & Swift, 1972) provide evidence of complexation between phenobarbital and phosphatidylcholine. We have been unable to crystallize this complex, but we have obtained crystal complexes of a barbiturate with hexamethylphosphoramide (Fig. 2). Thermodynamic properties of hexamethylphosphoramide in carbon tetrachloride solution (Arnett, Joris, Mitchell, Murty, Gorrie & Schleyer, 1970) show this molecule to be a particularly strong hydrogen-bonding acceptor. For the complex formed with *p*-fluorophenol as donor, the heat of formation of a hydrogen-bonded dimer is 8 kcal mole^{-1}. We now report the crystal structure determination of the 1:2 triclinic complex of hexamethylphosphoramide (Fig. 2) with barbital, and crystal data for a monoclinic complex.

Experimental

Crystal data for two complexes of hexamethylphosphoramide and barbital are given in Table 1. The monoclinic crystals were obtained as plates elongated along **c** by slow cooling to room temperature of a solution of barbital in liquid hexamethylphosphoramide. The triclinic crystals were obtained as needles elongated on **a**, from a solution of both components in absolute ethanol. In order to exclude atmospheric moisture, crystals of both complexes were grown in a sealed flask, and were coated in lacquer before X-ray data were measured. Otherwise, the crystals decomposed in a few hours. X-ray oscillation and Weissenberg photographs (Cu $K\alpha$ radiation) showed that the monoclinic complex has an unusually large unit cell. The crystal density (1·172 g cm^{-3}) corresponds to a total of 48 molecules per unit cell, or 12 molecules in the asymmetric unit if the space group has the lower symmetry *Cc*. The composition of this complex could not be established with confidence from the unit-cell volume and crystal density because the two components have similar molecular weights.

Table 1. *Crystal data for the complexes of hexamethylphosphoramide with barbital*

	Hexamethylphosphoramide $[(CH_3)_2N]_3PO$ M.W. 179·2 Triclinic,* m.p. 124°	Barbital $C_8H_{12}N_2O_3$ M.W. 184·2 Monoclinic m.p. 67°
Space group	$P\bar{1}$	*Cc* or *C*2/*c*
a	6·889 (1) Å	45·64 Å
b	12·568 (1)	20·29
c	17·944 (2)	13·91
α	75·76 (1)°	–
β	87·85 (1)	106·4°
γ	76·31 (1)	–
d_{meas}	1·246 g cm^{-3}	1·172 g cm^{-3}
d_{calc}	1·243 g cm^{-3}	1·172 g cm^{-3}
Z	2[$(CH_3)_2N]_3PO$ +4($C_8H_{12}N_2O_3$)	48 molecules with M.W. of 182

* The crystal data refer to the Niggli reduced cell, which was used throughout the structure determination.

The crystal structure determination of the triclinic form was undertaken first because of its relative simplicity. A needle-shaped crystal was cut to give dimensions 0·29 × 0·29 × 0·15 mm and was mounted with the a axis approximately along the φ axis of a computer-controlled four-circle diffractometer. Unit-cell dimensions and the integrated intensities for 6020 reflections with $\theta \leq 75°$ were measured with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Reflections were scanned in the $\theta/2\theta$ mode with θ scan width $(0{\cdot}6 + 0{\cdot}3 \tan\theta)°$. There were 1316 weak reflections for which the intensity I was less than $2{\cdot}0\sigma(I)$. These reflections were assigned intensities of $\sigma(I)/2$. No corrections were made for X-ray absorption and extinction.

The phase problem was solved by the heavy-atom method, based on the phosphorus atoms. Atomic parameters (Table 2) were refined by a block-diagonal

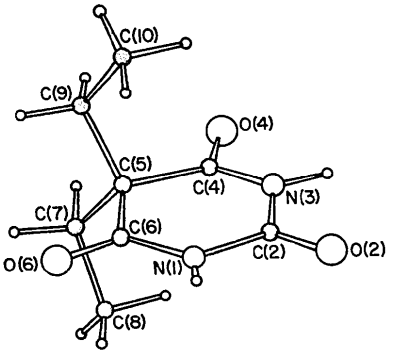

Fig. 1. Atomic nomenclature and conformation of barbital.

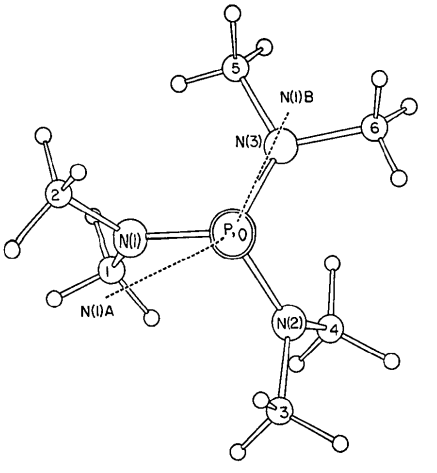

Fig. 2. The hexamethylphosphoramide molecule viewed down the phosphoryl bond. The dotted lines are the projections of the hydrogen bonds which are formed at the phosphoryl oxygen atom.

least-squares procedure in which the function minimized was $\sum_H w_H \Delta_H^2$, where $\Delta_H = |F_H^{obs}| - |F_H^{calc}|$. The weights were given by $w_H^{-1} = 0{\cdot}1 + 0{\cdot}002|F_H|^2$. The atomic scattering factors were those of Cromer & Waber (1965) for phosphorus (including $\Delta f' = 0{\cdot}2$), oxygen, nitrogen and carbon, and of Stewart, Davidson & Simpson (1965) for hydrogen. All hydrogen atomic positions were obtained from a difference Fourier map which was computed after refinement of anisotropic temperature factors had been made for the non-hydrogen atoms. Hydrogen atom positional parameters were then refined, but hydrogen atom thermal parameters were fixed with values the same as those of the atoms to which they are bonded. During the final cycles of least-squares calculation, reflections with $I < 2\sigma(I)$ and two strong reflections for which $|F_H^{calc}| > |F_H^{obs}|$ were given zero weight. The final R index* was 0·062 for all reflections and 0·046 for reflections with non-zero weight.†

Discussion

The crystal structure determination shows a hydrogen-bonded 1:2 complex with one hexamethylphosphoramide molecule and two barbital molecules (*A* and *B*) in the asymmetric unit of space group $P\bar{1}$.

In both barbital molecules, the oxopyrimidine ring

* $R = \sum_H |\Delta_H| / \sum_H |F_H^{obs}|$.

† The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30367 (32pp., 1 microfiche). Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England,

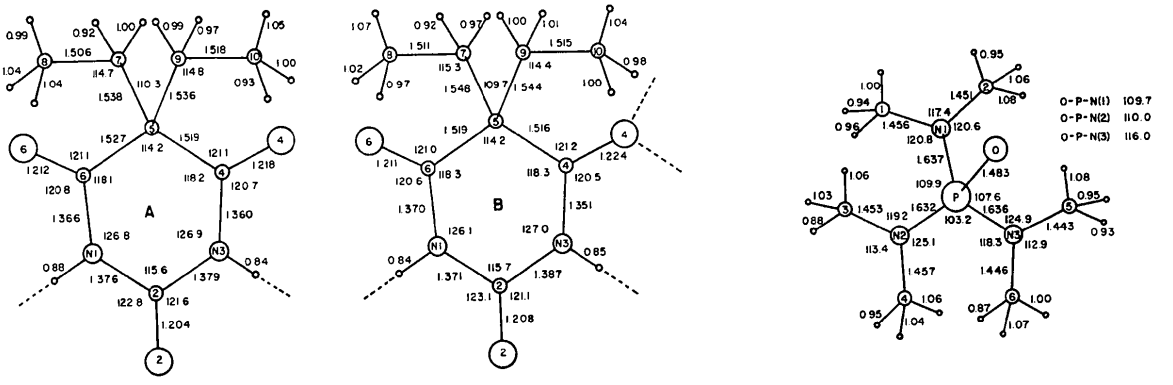

Fig. 3. Bond lengths and angles. The e.s.d.'s are 0·005 Å in C–N, C=O and C–C bond lengths, 0·3° in corresponding bond angles. 0·003 Å in P–N and P–O bond lengths, and 0·2° in corresponding angles, and 0·05 Å in bond lengths involving hydrogen atoms.

Table 2. *Atomic parameters and their e.s.d.'s*

Positional parameters are given as fractions of the unit-cell translations ($\times 10^4$) for non-hydrogen atoms and ($\times 10^3$) for hydrogen atoms. Anisotropic thermal factors ($\times 10^4$) are given by the expression $T = \exp[-\sum(\beta_{ij} h_i h_j)]$. The e.s.d.'s which are given in parentheses refer to the least significant digit in the corresponding parameters.

(*a*) Hexamethylphosphoramide

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	1097 (1)	−21 (1)	3015 (1)	201 (2)	47 (1)	24 (1)	−21 (1)	−1 (1)	−6 (1)
O	1386 (4)	1138 (2)	2707 (1)	338 (8)	47 (2)	32 (1)	−27 (3)	21 (2)	−7 (1)
N(1)	−1274 (5)	31 (3)	3176 (2)	193 (7)	91 (3)	48 (1)	−29 (4)	1 (3)	−16 (2)
N(2)	2403 (5)	−622 (3)	3811 (2)	249 (8)	79 (3)	26 (1)	−19 (3)	−8 (2)	−7 (1)
N(3)	1869 (5)	−907 (3)	2474 (2)	256 (8)	66 (2)	36 (1)	−17 (3)	−8 (2)	−20 (1)
C(1)	−1903 (8)	−905 (6)	3700 (3)	291 (13)	185 (7)	50 (2)	−125 (8)	14 (4)	−12 (3)
C(2)	−2804 (8)	895 (5)	2693 (6)	276 (14)	97 (5)	145 (6)	−20 (6)	−79 (7)	−24 (4)
C(3)	2479 (7)	34 (5)	4368 (3)	301 (12)	160 (6)	39 (2)	−14 (7)	−13 (4)	−40 (3)
C(4)	3066 (8)	−1836 (4)	4127 (3)	369 (14)	95 (4)	41 (2)	−22 (6)	−21 (4)	21 (2)
C(5)	599 (8)	−1206 (4)	1977 (3)	399 (14)	100 (4)	42 (2)	−86 (6)	−3 (4)	−28 (2)
C(6)	3963 (7)	−1099 (4)	2244 (3)	291 (11)	86 (3)	43 (2)	−4 (5)	4 (3)	−28 (2)

	x	y	z		x	y	z
H(11)	−100 (7)	−134 (5)	415 (3)	H(41)	225 (7)	−212 (4)	453 (3)
H(12)	−250 (7)	−127 (5)	340 (3)	H(42)	451 (7)	−200 (4)	435 (3)
H(13)	−311 (7)	−60 (5)	393 (3)	H(43)	291 (7)	−227 (4)	370 (3)
H(21)	−225 (8)	144 (4)	235 (4)	H(51)	56 (7)	−69 (4)	140 (3)
H(22)	−372 (8)	121 (4)	311 (4)	H(52)	104 (7)	−198 (4)	197 (3)
H(23)	−338 (8)	42 (4)	237 (4)	H(53)	−68 (7)	−114 (4)	217 (3)
H(31)	150 (7)	−20 (4)	482 (3)	H(61)	412 (7)	−64 (4)	172 (3)
H(32)	391 (7)	−5 (4)	457 (3)	H(62)	452 (6)	−197 (4)	225 (3)
H(33)	221 (7)	75 (5)	412 (3)	H(63)	465 (6)	−97 (4)	260 (3)

Table 2 (*cont.*)

(*b*) Barbital (molecule *A*, above; molecule *B*, below)

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(2)	−1581 (5)	3553 (3)	1570 (2)	398 (10)	97 (3)	32 (1)	3 (4)	5 (2)	−21 (1)
	3330 (5)	3528 (3)	1926 (2)	486 (11)	103 (3)	30 (1)	−113 (4)	27 (3)	−26 (1)
O(4)	−5269 (6)	6091 (3)	2749 (2)	437 (11)	70 (2)	46 (1)	58 (4)	−16 (3)	−11 (1)
	4764 (4)	4112 (2)	−587 (1)	275 (6)	55 (2)	25 (1)	−53 (3)	0 (2)	−4 (1)
O(6)	−499 (5)	2898 (2)	4124 (2)	332 (8)	82 (2)	32 (1)	19 (3)	−13 (2)	−4 (1)
	2045 (5)	1040 (2)	692 (2)	355 (8)	65 (2)	39 (1)	−89 (3)	9 (2)	−10 (1)
N(1)	−1039 (5)	3244 (2)	2852 (2)	259 (8)	55 (2)	31 (1)	4 (3)	1 (2)	−9 (1)
	2805 (4)	2241 (2)	1312 (2)	247 (7)	51 (2)	26 (1)	−41 (3)	14 (2)	−6 (1)
C(2)	−1932 (6)	3859 (3)	2157 (2)	268 (9)	59 (3)	29 (1)	−21 (4)	5 (3)	−9 (1)
	3366 (6)	3205 (3)	1344 (2)	258 (9)	60 (2)	26 (1)	−45 (4)	7 (2)	−11 (1)
N(3)	−3301 (5)	4851 (2)	2173 (2)	289 (8)	54 (2)	27 (1)	−9 (3)	−10 (2)	−3 (1)
	4004 (5)	3798 (2)	658 (2)	285 (8)	52 (2)	26 (1)	−58 (3)	5 (2)	−11 (1)
C(4)	−3952 (6)	5234 (2)	2806 (2)	284 (10)	50 (2)	32 (1)	−5 (4)	−4 (3)	−7 (1)
	4135 (5)	3524 (2)	−27 (2)	174 (7)	40 (2)	24 (1)	−18 (3)	−5 (2)	−5 (1)
C(5)	−2961 (6)	4580 (3)	3578 (2)	273 (10)	59 (3)	29 (1)	3 (4)	−10 (3)	−13 (1)
	3516 (5)	2463 (2)	−77 (2)	191 (7)	43 (2)	25 (1)	−26 (3)	−5 (2)	−8 (1)
C(6)	−1392 (5)	3508 (3)	3547 (2)	237 (9)	55 (2)	29 (1)	−14 (4)	1 (3)	−6 (1)
	2707 (5)	1859 (3)	665 (2)	189 (7)	44 (2)	29 (1)	−24 (3)	−2 (2)	−6 (1)
C(7)	−4595 (7)	4242 (4)	4130 (2)	309 (12)	100 (4)	29 (1)	28 (5)	9 (3)	−9 (2)
	5393 (6)	1640 (3)	−262 (2)	271 (9)	52 (2)	35 (1)	−22 (4)	18 (3)	−15 (1)
C(8)	−5556 (8)	3384 (5)	3933 (3)	316 (13)	144 (6)	49 (2)	−62 (7)	5 (4)	3 (3)
	7034 (7)	1196 (4)	329 (3)	222 (10)	83 (3)	63 (2)	13 (5)	−3 (4)	−18 (2)
C(9)	−1937 (9)	5356 (4)	3879 (3)	447 (17)	76 (3)	64 (2)	−5 (6)	−51 (5)	−31 (2)
	1904 (6)	2770 (3)	−719 (2)	294 (10)	74 (3)	32 (1)	−62 (5)	−32 (3)	−3 (2)
C(10)	−421 (11)	5827 (5)	3342 (5)	466 (21)	94 (5)	132 (5)	−73 (8)	−58 (8)	−29 (4)
	80 (7)	3671 (5)	−624 (3)	232 (11)	111 (4)	64 (2)	−34 (5)	−43 (4)	7 (3)

	x	*y*	*z*		*x*	*y*	*z*
H(1)	−27 (6)	258 (3)	285 (2)	H(83)	−448 (7)	263 (5)	396 (3)
	236 (6)	189 (3)	171 (2)		817 (6)	69 (4)	17 (3)
H(3)	−380 (6)	520 (3)	174 (2)	H(91)	−133 (8)	493 (4)	439 (3)
	437 (6)	440 (3)	66 (2)		252 (6)	304 (3)	−122 (2)
H(71)	−405 (7)	394 (4)	467 (2)	H(92)	−286 (8)	603 (4)	396 (3)
	498 (6)	100 (3)	−38 (2)		146 (6)	206 (3)	−72 (2)
H(72)	−552 (7)	490 (4)	415 (2)	H(101)	−131 (9)	637 (5)	287 (4)
	578 (6)	205 (3)	−74 (2)		43 (7)	443 (4)	−61 (3)
H(81)	−661 (7)	322 (5)	431 (3)	H(102)	1 (9)	631 (5)	364 (4)
	651 (6)	68 (4)	82 (3)		−82 (7)	384 (4)	−107 (3)
H(82)	−607 (7)	366 (4)	336 (3)	H(103)	48 (9)	530 (5)	314 (4)
	747 (6)	183 (4)	49 (3)		−40 (7)	338 (4)	−10 (3)

is almost planar and the ethyl carbon atoms and atom C(5) form an almost fully extended chain at right angles to the ring. The slight ring puckerings in molecules *A* and *B* closely resemble those found in molecules *C* and *D* in polymorph IV of barbital (Craven & Vizzini, 1971; Craven, Cusatis, Gartland & Vizzini, 1973). The greatest atomic displacements from the best least-squares planes through the six ring atoms are 0·07 Å for atom O(2) in molecule *A* and 0·11 Å for atom O(6) in molecule *B*. The torsion angles in the chain C(10)–C(9)–C(5)–C(7)–C(8) in molecules *A* and *B* respectively are −174·8 (5)° and −173·7 (4)° about the bond C(9)–C(5) and −174·0 (5)°, −175·4 (3)° about the bond C(5)–C(7).

There is good agreement between the bond lengths and angles of molecules *A* and *B* (Fig. 3). The differences between bond lengths such as C(4)–O(4) and C(6)–O(6) in molecule *B* are too small (0·013 Å) to be highly significant in terms of their e.s.d.'s (0·004 Å). However, this bond-length difference has the same sense and order of magnitude as have been consistently observed in other barbiturate molecules in which O(4) is hydrogen bonded, while O(6) is not (Craven, Cusatis, Gartland & Vizzini, 1973). In molecule *A*, where none of the barbiturate oxygen atoms is hydrogen bonded, bond-length differences across the C(2)···C(5) axis are even smaller than in molecule *B*.

The hexamethylphosphoramide molecule shows marked departures from threefold rotational symmetry about the P=O bond. This asymmetry involves the P–N torsion angles (Fig. 2) and valence bond angles (Fig. 3), but not bond lengths (Fig. 3). The torsion angles O–P–N(1)–C(2), O–P–N(2)–C(3) and O–P–N(3)–C(6) are all different (32·8°, 41·3°, 56·3°, e.s.d. 0·4°), in a way which appears to be uncorrelated with differences among the three O–P–N, the three N–P–N, and the six P–N–C bond angles. The bonds at the three nitrogen atoms are almost planar, but each is significantly displaced (0·09, 0·13, and 0·17 Å) from the plane through the phosphorus and methyl carbon atoms to which it is bonded. The nitrogen atoms N(1) and N(2) are on the same side of the plane as the phosphoryl oxygen atom, but nitrogen atom N(3) is on the opposite side.

The bond lengths in hexamethylphosphoramide (Fig. 3) are similar to those reported in crystal structure determinations of related molecules, such as *N,N*-dimethyldiphenylphosphinamide [P–O, 1·47 Å; P–N, 1·67 Å; N–CH_3, 1·52 and 1·47 Å; Haque & Caughlan (1966)], the trimeric diethylamide of metaphosphoric acid [mean P=O bond length 1·44 Å, mean P–N bond length 1·67 Å; Andrianov, Bokii, Cherepinskii-Malov, Tarnopolskii & Struchkov (1969)], 2,4,5-trimethoxy-1,3,5-trimethyl-2,4,6-trioxotriphosphazane [mean phosphoryl P=O bond length 1·46 Å, mean P–N bond length 1·66 Å; Ansell & Bullen (1968)] and triethylene thiophosphoramide [mean P–N bond length 1·64 Å; Subramanian & Trotter (1969)]. The phosphoryl bond length in hexamethylphosphoramide (1·483 Å) is nearly the same as the phosphodiester phosphoryl bond lengths found in glycerylphosphorylcholine [mean value 1·486 Å; Abrahamsson & Pascher (1966)] and glycerylphosphorylethanolamine monohydrate [mean value 1·488 Å; De Titta & Craven (1973)]. Since it appears that these phosphoryl bonds have similar double-bond character, the phosphoryl oxygen atom in hexamethylphosphoramide should have similar affinity as a hydrogen-bonding acceptor to the phosphoryl oxygen atoms of phospholipids.

In the 1:2 complex of hexamethylphosphoramide with barbital there are hydrogen-bonded chains which are parallel to **a** and have the thickness of one unit cell in the **b** and **c** directions (Fig. 4). Non-polar methyl or methylene groups from both kinds of molecules form the outer surface of each chain. Each barbital molecule *A* and *B* is the donor in one hydrogen bond to the O(4) oxygen atom of a barbital *B* molecule, and is also donor in a second hydrogen bond to the hexamethylphosphoramide oxygen atom. The hydrogen bonds N(3,*A*)H···O(4,*B*) and N(3,*B*)H···O(4,*B*) respectively have N···O distances 2·93 and 2·92 Å, H···O distances 2·10 and 2·07 Å, and N–H···O angles 171° and 177°. The N(3,*A*)···O(4,*B*)···N(3,*B*) angle is 86·0°. The hydrogen bonds N(1,*A*)H···O=P and N(1,*B*)H···O=P respectively have N···O distances 2·84 and 2·81 Å, H···O distances 1·97 and 1·98 Å and N–H···O angles 173° and 176°. The N(1,*A*)···O···N(1,*B*) angle is 89·5°. Thus, the arrangement of pairs of hydrogen bonds at the carbonyl O(4) and phosphoryl oxygen atoms is very similar except that the latter hydrogen bonds are shorter by about 0·1 Å.

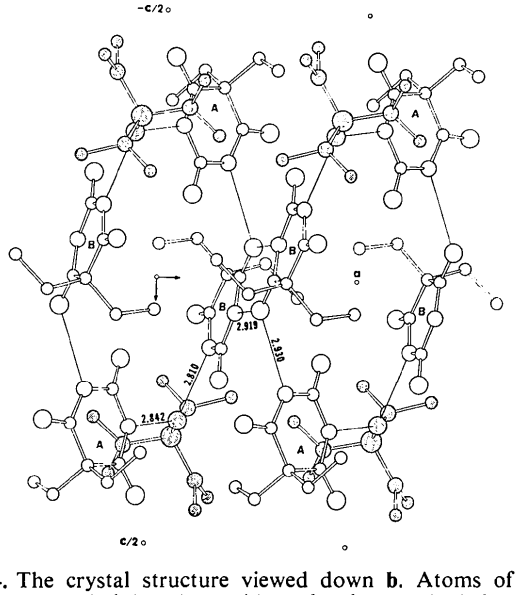

Fig. 4. The crystal structure viewed down **b**. Atoms of the hexamethylphosphoramide molecules are shaded.

The N···O distances for the hydrogen bonds involving only barbital are near the center of the range (2·81 to 2·98 Å) which has been observed for all such hydrogen bonds (Gartland & Craven, 1974). The N···O distances for the hydrogen bonds involving the phosphoryl oxygen are near the short limit of this range, but are longer than the NH···O=C hydrogen bond in which barbital is donor and aminopyridine is acceptor (2·75 Å; Kiryu, 1971). They are also longer than one of the NH···O=P hydrogen bonds (N···O distances 2·71, 2·85 Å) in glycerylphosphorylethanolamine monohydrate (DeTitta & Craven, 1973). Thus, in the 1:2 complex of hexamethylphosphoramide and barbital, the N···O distances are consistent with strong NH···O=P hydrogen bonds, but these do not appear to be markedly stronger than some hydrogen bonds in related crystal structures. We note that NH···O=C hydrogen bonds between barbiturate molecules have N···O distances which differ over a range of almost 0·2 Å, presumably as a result of crystal packing effects. The two NH···O=P hydrogen bonds in the triclinic complex of hexamethylphosphoramide with barbital do not provide an adequate estimate of the range of N···O distances which is to be expected for such hydrogen bonds. However, the crystal structure determination of the monoclinic complex (in progress) should give considerably more data concerning the nature of NH···O=P hydrogen bonds involving barbiturates.

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The Crystal Structure of 1,4-Diiodobicyclo[2,2,2]octane

BY DOYLE BRITTON*

Laboratory for Organic Chemistry, Swiss Federal Institute of Technology, 8006 *Zürich, Switzerland*

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1,4-Diiodobicyclo[2,2,2]octane is tetragonal, probable space group $P4_12_12_1$, with $a=6{\cdot}653$ and $c=23{\cdot}311$ Å, $Z=4$. The structure, determined from Fourier maps and partial least-squares refinement, gave a final conventional R value of 0·045 for a disordered model with assumed tetrahedral bond angles and normal C–C bond lengths. The disorder arises from the molecules being rotated $\pm 20°$ about the three-fold molecular axis (*i.e.* the I···I axis) away from an orientation appropriate to the space-group symmetry. A less probable alternative structure requiring twinned crystals with space group $P4_1$ fits the data equally well.

Introduction

The packing of diiodoacetylene (Dunitz, Gehrer & Britton, 1972) shows unusual features, and it was thought that diiodobicyclooctane, which is another diiodide molecule with approximately cylindrical symmetry, would be worth examining. Accordingly, its structure is reported here.

Experimental

A sample of the compound, which had previously been provided for another purpose by Dr J. C. Kauer of the Central Research Department of E. I. du Pont de Nemours and Co., Inc. (*Chem. Eng. News*, 1970), was recrystallized from carbon tetrachloride. The crystals, mostly thin, square plates with no extinction perpendicular to the plate direction, were not well enough formed for any useful conclusions to be drawn about the crystallographic point group. Precession photographs showed the crystals to be tetragonal with Laue symmetry $4/mmm$. Systematic extinctions ($h00$, $h\neq 2n$; $00l$, $l\neq 4n$) indicate the space group to be $P4_12_12$ (No. 92) or its enantiomorph. The cell constants, determined from a least-squares fit of the diffractometer positions of 20 peaks (Mo $K\alpha$ radiation, $\lambda=0{\cdot}71069$ Å), are $a=6{\cdot}653$, $c=23{\cdot}311$ Å; the estimated error is less than 0·1%. For $Z=4$ the molecular volume is 258 Å^3 and the calculated density is 2·329 g cm^{-3}. The linear absorption coefficient is 61·0 cm^{-1} (Mo $K\alpha$).

A crystal $0{\cdot}10\times 0{\cdot}15\times 0{\cdot}20$ mm was used for intensity measurements. It was mounted on the end of a fine glass fibre, which was then sealed in a thin-walled glass capillary. Data were collected at room temperature using a 4-circle Hilger and Watts Y290 diffractometer with monochromatic Mo $K\alpha$ radiation. One complete octant of data (1295 reflexions) was collected for θ between 0 and 26°. Reflexions between 0 and 20° were scanned in 80 steps of 0·01° in θ and ω with 1 s counting times per step and 10 s background counts at each end of the scan; for 20–26° 100 such steps were used and the background counting time was increased to 25 s at each end. The 50 most intense reflexions were also scanned using reduced intensity to test for saturation of the counter and the seven most intense reflexions were corrected for this effect. The intensities of two check reflexions were measured every 25 reflexions; although the crystal turned dark yellow with use, there was no variation with time of the intensities of the check reflexions and the average deviation from the mean was 1·1%.

* Permanent address: Chemistry Department, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.