BUSING, W. R., SMITH, H. G., PETERSON, S. W. & LEVY, H. A. (1964). *J. Phys. Radium*, **25**, 495.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71.
HARKEMA, S., BATS, J. W., WEYENBERG, A. M. & FEIL, D. (1972). *Acta Cryst.* B**28**, 1646.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
MOOTZ, D. & ALBRAND, K.-R. (1972). *Acta Cryst.* B**28**, 2459.
Neutron Diffraction Commission (1969). *Acta Cryst.* A**25**, 391.
PRYOR, A. W. & SANGER, P. L. (1970). *Acta Cryst.* A**26**, 543.
SUNDERA-RAO, R. V. G., TURLEY, J. W. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 435.
WOLFRAM, W., ARUTUNIAN, E. G., ANTISHKINA, A. S. & PORAI-KOSHITS, M. A. (1967). *Bull. Acad. Polonaise Sci. Sér. Sci. Chim.* **15**, 83.
World List of Crystallographic Computer Programs (1972). 3rd Edition. To be published.
WORSHAM, J. E. & BUSING, W. R. (1969). *Acta Cryst.* B**25**, 572.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.

Acta Cryst. (1972). B**28**, 2459

An X-ray Structure Redetermination of the Urea–Phosphoric Acid Compound*

BY DIETRICH MOOTZ AND KARL-RICHARD ALBRAND

Max-Planck-Institut für Festkörperforschung, 7 Stuttgart 1, Heilbronner Str. 69, Germany (BRD)

(*Received* 21 *March* 1972)

The crystal structure of the urea–phosphoric acid compound $CO(NH_2)_2.H_3PO_4$ has been redetermined ($Pbca$; $z=8$; $a=17\cdot6508$, $b=7\cdot4817$, $c=8\cdot9991$ Å). With a very short and nearly centred hydrogen bond from the acid to the oxygen atom of the base the structure is between that of a true adduct and that of an onium salt. All hydrogen atoms were located; with 1126 independent Cu $K\alpha$ counter data the final R value is 0·031.

As part of our program to study the structural behaviour of the acid proton in crystalline acid/base syssystems (*e.g.* Altenburg & Mootz, 1971; Mootz & Altenburg, 1971) we have carried out an accurate crystal structure determination of the urea–phosphoric acid compound. Earlier investigations by Sundera-Rao, Turley & Pepinsky (1957) and by Wolfram, Arutunian, Antishkina & Porai-Koshits (1967) revealed a very strong hydrogen bond between the acid and the oxygen atom of the urea moiety (O···O distance 2·414 Å and 2·45 Å respectively), but did not decide between nor comment on the structural alternatives of a true adduct and an onium salt. In order to study this aspect of the structure in detail, which requires a knowledge of the hydrogen atom positions as well as more accurate interatomic distances and angles of the heavy atoms, we decided to collect new X-ray data and repeat the analysis.

After we had finished the refinement we learned from the title programme of a meeting of a recent neutron diffraction study of the same compound by Busing & Kostansek (1971). This work has now been published in detail (Kostansek & Busing, 1972). Apart from being more accurate in hydrogen atom positions and thermal parameters, it is in good agreement with our own study, the presentation of which can therefore be kept short.

Experimental and crystallographic data

The urea–phosphoric acid compound crystallizes in space group $Pbca$ with eight formula units $CO(NH_2)_2.H_3PO_4$ per unit cell. A least-squares refinement of angular measurements on a diffractometer yielded the improved lattice parameters $a=17\cdot6508$ (9), $b=7\cdot4817$ (4) and $c=8\cdot9991$ (7) Å. The intensities of 1126 independent reflexions with $\theta<70°$ were measured with Ni-filtered Cu $K\alpha$ radiation on a tape-controlled Siemens automatic diffractometer in the $\theta/2\theta$ mode. No correction for absorption was applied ($\mu_{\text{Cu }K\alpha}=38\cdot9\ \text{cm}^{-1}$).

Refinement of the structure

Least-squares refinement was started from the heavy atom parameters of Sundera-Rao, Turley & Pepinsky (1957). The seven hydrogen atoms could be located in a difference Fourier map. After an empirical correction of the thirteen strongest intensities for extinction, anisotropic treatment of all atoms converged to an unweighted R value of 0·031. The observations were weighted according to $w=1$ for $|F_o|<K$ and $w=K^2/|F_o|^2$ for $|F_o|\ge K$ with $K=20$. The form factors used

---

* Short version of a part of the dissertation of K.-R. Albrand, Techn. Universität Braunschweig, (1972).

were those of Hanson, Herman, Lea & Skillman (1964) for P, O, N, C, and of Stewart, Davidson & Simpson (1965) for H. The final parameters are listed in Table 1, the observed and calculated structure factors in Table 2. Fig. 1 is a complementary drawing of the Fourier synthesis and difference Fourier synthesis with the heavy and hydrogen atom electron density maxima, respectively. Labeling of the atoms is according to Kostansek & Busing (1972).

Results and discussion

The bond lengths of the acid and base moieties (Table 3) lie between those of H_3PO_4 (phosphoric acid: Cole, 1966) and $H_2PO_4^-$ (*e.g.* calcium dihydrogenphosphate monohydrate: Dickens & Bowen, 1971) as well as between those of $CO(NH_2)_2$ (urea: Pryor & Sanger, 1970) and $(NH_2)_2COH^+$ (uronium nitrate: Worsham & Busing, 1969). The very strong hydrogen bond $O(4)\cdots H(4)\cdots O(5)$ between both groups [$O\cdots O$ distance 2·424 (2) Å] is more or less centred, *i.e.* the proton transition from the acid to the base is only partial. Thus from heavy atom *and* hydrogen atom positions the compound is neither a true adduct, $CO(NH_2)_2.H_3PO_4$, nor a true onium salt, $(NH_2)_2COH^+H_2PO_4^-$, but of an intermediate nature.

Fig. 2. shows the asymmetric unit and its surrounding. Hydrogen bonding of all protons generates a complex three-dimensional network in the crystal structure. Pertinent distances and angles are listed in Table 4.

With mean and maximum differences of 0·9 and 2·3σ, respectively, the heavy atom coordinates agree well with those of the neutron diffraction study by Kostansek & Busing (1972). This is reflected by an equally good agreement between heavy-atom interatomic distances and angles in both analyses. For the hydrogen coordinates, on the other hand, mean and maximum differences of 2·3 and 6·0σ point to a systematic difference between the two experiments. In fact whereas the bond angles involving hydrogen are generally in fair agreement most of the O–H and N–H distances are shorter in the X-ray than in the neutron work. This is to be expected if the electron density of a hydrogen atom is displaced from its nucleus toward the heavy atom.

The diagonal elements of the temperature coefficients for the heavy atoms are all larger in the X-ray work than in the neutron study, suggesting that the electron distribution is more diffuse than the X-ray scattering factors indicate. It is not surprising that the thermal parameters for hydrogen are not in good agreement.

Most of the final calculations were done with the X-ray 63 system (Stewart & High, 1965). Fig. 2 was prepared with the program *ORTEP* (Johnson, 1965). This research was supported by the Deutsche For-

Table 1. *The atomic parameters and their standard deviations*

The B_{ij} are consistent with the temperature factor in the form $f_T = \exp[-\frac{1}{4}(B_{11}h^2a^{*2} + 2B_{23}klb^*c^* + \ldots)]$. Most of the hydrogen thermal parameters did not stay positive definite. Therefore only the averages B of the diagonal coefficients are listed.

	x	y	z
P	0·31089 (3)	0·27860 (6)	0·30906 (5)
O(1)	0·33934 (9)	0·09142 (24)	0·36017 (23)
O(2)	0·27753 (8)	0·38453 (18)	0·43567 (14)
O(3)	0·24654 (9)	0·25121 (24)	0·19343 (17)
O(4)	0·37947 (9)	0·36575 (21)	0·23808 (17)
O(5)	0·44703 (10)	0·63402 (23)	0·31060 (18)
N(1)	0·50754 (12)	0·78258 (31)	0·49107 (31)
N(2)	0·39673 (12)	0·63569 (31)	0·54195 (26)
C	0·44998 (11)	0·68374 (26)	0·44638 (21)

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
P	1·59 (2)	1·57 (2)	1·47 (2)	−0·01 (1)	0·01 (1)	−0·12 (1)
O(1)	2·30 (7)	2·02 (7)	3·70 (8)	−0·01 (5)	−0·18 (6)	0·21 (6)
O(2)	2·45 (6)	2·14 (5)	1·79 (6)	0·12 (4)	0·18 (4)	−0·12 (4)
O(3)	2·27 (6)	3·76 (7)	2·18 (6)	0·38 (5)	−0·50 (5)	−0·75 (5)
O(4)	2·77 (6)	2·69 (6)	2·44 (6)	−0·73 (5)	0·81 (5)	−0·40 (5)
O(5)	3·51 (7)	2·96 (7)	2·20 (7)	−1·15 (6)	0·32 (5)	−0·15 (5)
N(1)	2·51 (9)	3·12 (9)	2·73 (10)	−0·84 (7)	0·26 (8)	−0·38 (8)
N(2)	2·88 (9)	3·85 (10)	2·63 (10)	−1·12 (7)	0·70 (7)	−0·79 (7)
C	2·17 (8)	1·72 (7)	2·18 (8)	0·08 (6)	0·01 (6)	0·01 (6)

	x	y	z	B
H(1)	0·305 (2)	0·028 (4)	0·390 (4)	4·4
H(3)	0·256 (2)	0·202 (4)	0·101 (4)	4·4
H(4)	0·411 (2)	0·505 (6)	0·281 (3)	8·6
H(11)	0·540 (2)	0·808 (4)	0·434 (4)	2·9
H(12)	0·510 (2)	0·809 (5)	0·579 (3)	4·1
H(21)	0·361 (2)	0·560 (5)	0·513 (3)	4·7
H(22)	0·401 (1)	0·681 (4)	0·636 (3)	3·1

Table 2. *The observed and calculated structure factors*

Within each group of reflexions the columns are 1, $10|F_o|$ and $10F_c$. The 13 strongest intensities, which were corrected empirically for extinction, and the 15 reflexions with $I < 1{\cdot}5\sigma_I$ are marked E and *, respectively.

0,0,L		
2	562	-555E
4	603	600
6	413	406
8	664	-709
10	192	190
0,2,L		
0	1882	-1962E
1	224	219
2	421	422
3	31	-50
4	502	-494
5	765	809
6	458	-470
7	27	25
8	480	499
9	10	3
10	334	-331
0,4,L		
0	394	-373
1	515	-535
2	281	-272
3	243	248
4	30	33
5	276	287
6	458	468
7	159	-163
8	173	-176
9	74	67
0,6,L		
0	351	-370
1	297	300
2	230	226
3	306	-304
4	140	140
5	456	-460
6	229	-228
7	295	288
8	119	118
0,8,L		
0	273	278
1	247	-245
2	170	-161
3	109	105
4	77	67
5	13	17
1,0,L		
2	1008	1066E
4	170	-194
6	154	155
8	20	13
10	247	-258
1,1,L		
1	344	-352
2	73	-80
3	49	-46
4	54	60
5	202	-204
6	118	117
7	178	183
8	6*	-12
9	134	136
10	49	52
1,2,L		
1	124	135
2	58	45
3	197	-187
4	246	259
5	63	57
6	252	-253
7	245	251
8	54	34
9	94	93
10	124	126
1,3,L		
1	352	355
2	46	-40
3	201	-213
4	540	-551
5	157	143
6	158	162
7	191	-192
8	160	-154
9	188	-193
10	89	-86
1,4,L		
1	104	107
2	200	-197
3	478	-498
4	266	-268
5	250	247
6	157	149
7	32	-23
8	32	-31
9	29	22
1,5,L		
1	27	23
2	212	-225
3	259	269
4	313	316
5	12	12
6	130	-128
7	81	77
8	69	68
9	37	37
1,6,L		
1	65	-63
2	200	-210
3	429	428
4	64	63
5	404	-397
6	18	4
7	97	91
8	44	-39
1,7,L		
1	139	-136
2	129	132
3	120	-123
4	100	103
5	10	-0
6	60	53
7	107	-101
1,8,L		
1	114	117
2	17	22
3	171	-169
4	57	51
5	255	252
1,9,L		
1	36	31
2,0,L		
0	689	-676E
2	1000	1069E
4	485	472
6	54	-43
8	430	438
10	163	-167
2,1,L		
0	727	719E
1	404	-391E
2	963	-979
3	625	622
4	65	27
5	294	-296
6	62	42
7	14	17
8	80	-51
9	148	145
10	134	141
2,2,L		
0	287	283
1	570	-567
2	1196	-1232E
3	112	-105
4	104	-102
5	199	-206
6	223	228
7	281	-287
8	402	-411
9	270	281
10	242	242
2,3,L		
0	23	-31
1	689	703
2	61	53
3	407	-401
4	167	-176
5	113	119
6	291	-286
7	72	72
8	337	339
9	161	-160
10	221	-221
2,4,L		
0	416	-427
1	393	395
2	820	849
3	68	-72
4	43	-28
5	116	-119
6	296	-298
7	197	197
8	326	322
9	147	-153
2,5,L		
0	355	371
1	291	-294
2	50	47
3	99	-99
4	105	-96
5	153	155
6	272	271
7	215	-208
8	250	-244
9	79	84
2,6,L		
0	507	520
1	158	-150
2	185	-185
3	165	164
4	35	-33
5	120	120
6	75	70
7	109	-109
8	233	-223
2,7,L		
0	275	-273
1	65	34
2	40	36
3	22	18
4	24	20
5	22	-18
6	19	-16
2,8,L		
0	168	-169
1	178	180
2	80	-76
3	90	-85
4	18	-11
5	23	-21
2,9,L		
0	45	-41
1	170	-160
3,0,L		
2	26	-20
4	748	-709
6	104	-100
8	19	-21
10	28	-24
3,1,L		
1	17	17
2	1252	1243E
3	584	559
4	445	-449
5	54	47
6	566	545
7	125	-116
8	93	95
9	49	-41
10	156	-161
3,2,L		
1	1215	1207E
2	188	-190
3	84	-85
4	126	-71
5	259	259
6	79	-77
7	342	-357
8	16	14
9	156	-153
10	10	7
3,3,L		
1	298	-304
2	114	106
3	71	-68
4	420	425
5	185	-185
6	412	-405
7	25	23
8	116	111
9	13	12
10	72	68
3,4,L		
1	244	-250
2	146	148
3	69	72
4	374	386
5	183	-182
6	142	147
7	105	108
8	10	-12
9	34	29
3,5,L		
1	273	278
2	149	152
3	492	-498
4	335	-342
5	418	424
6	83	81
7	40	42
8	52	-52
9	86	74
3,6,L		
1	126	-130
2	54	52
3	69	-65
4	79	75
5	63	60
6	60	54
7	60	49
8	6*	2
3,7,L		
1	125	-121
2	182	-184
3	228	226
4	134	136
5	399	-383
6	4*	-4
3,8,L		
1	50	-51
2	59	-57
3	90	87
4	217	-209
5	54	-55
3,9,L		
1	151	148
4,0,L		
0	460	457
2	540	532
4	37	-3
6	251	243
8	350	-362
10	214	218
4,1,L		
0	2073	-2048E
1	404	-402
2	468	469
3	127	113
4	132	89
5	284	273
6	351	-332
7	41	42
8	615	627
9	67	-66
10	167	-169
4,2,L		
0	946	-948E
1	318	-311
2	55	-17
3	526	504
4	167	-160
5	312	-306
6	258	-260
7	47	55
8	79	65
9	86	-88
10	117	-119
4,3,L		
0	183	-173
1	54	-58
2	424	-432
3	24	23
4	188	180
5	24	25
6	173	172
7	93	-97
8	236	-236
9	116	119
10	200	204
4,4,L		
0	677	694
1	190	197
2	289	-282
3	90	97
4	292	290
5	50	38
6	114	112
7	41	-43
8	126	115
9	38	36
4,5,L		
0	16	-5
1	483	486
2	303	302
3	364	-366
4	61	62
5	385	-392
6	119	-117
7	167	170
8	39	41
4,6,L		
0	163	-167
1	138	135
2	66	58
3	198	-199
4	165	-167
5	62	58
6	14	-7
7	19	17
8	59	52
4,7,L		
0	205	219
1	361	-365
2	120	-123
3	295	287
4	77	-75
5	112	112
6	72	71
4,8,L		
0	13	15
1	119	-114
2	9	-1
3	49	-43
4	77	-72
5,0,L		
2	198	-192
4	670	653
6	267	276
8	20	-26
10	0*	-9
5,1,L		
1	169	184
2	653	-635
3	133	134
4	764	749
5	21	-28
6	351	-361
7	191	191
8	217	221
9	19	20
10	200	212
5,2,L		
1	170	-148
2	188	185
3	90	-83
4	484	-472
5	329	320
6	256	255
7	105	-100
8	106	-99
9	66	-73
10	82	-79
5,3,L		
1	123	-119
2	162	149
3	449	-447
4	512	-510
5	118	123
6	287	291
7	225	-228
8	30	-30
9	26	-26
10	121	-124
5,4,L		
1	483	-423
2	400	-403
3	178	181
4	325	325
5	92	-87
6	469	-476
7	51	47
8	105	103
9	96	97
5,5,L		
1	46	48
2	204	-208
3	438	445
4	232	225
5	227	-220
6	166	-160
7	93	87
8	41	-40
5,6,L		
1	210	217
2	312	313
3	18	18
4	180	-180
5	21	15
6	116	117
7	90	-85
5,7,L		
1	60	62
2	149	152
3	207	-204
4	61	-58
5	230	227
6	90	83
5,8,L		
1	46	37
2	49	11
3	13	-2
4	31	-28
6,0,L		
0	23	27
2	27	16
4	181	-170
6	414	411
8	160	157
10	170	177
6,1,L		
0	282	280
1	296	-294
2	400	389
3	499	-487
4	97	-86
5	30	-36
6	243	250
7	332	-338
8	269	-273
9	133	134
10	173	181
6,2,L		
0	73	-80
1	162	-154
2	194	-184
3	452	-445
4	240	-245
5	72	-72
6	162	-151
7	111	112
8	82	78
9	170	-170
10	136	-144
6,3,L		
0	519	-515
1	378	388
2	735	747
3	372	372
4	138	-102
5	44	43
6	292	-303
7	426	425
8	83	85
9	194	-201
6,4,L		
0	377	389
1	412	-420
2	181	181
3	26	-38
4	242	250
5	95	94
6	44	33
7	171	-173
8	177	-172
9	91	93
6,5,L		
0	427	434
1	227	-223
2	417	-422
4	139	135
5	13	-9
6	100	101
7	110	-110
8	101	-99
6,6,L		
0	267	-274
1	296	295
2	31	34
3	43	43
4	51	44
5	89	83
6	113	-103
7	170	166
6,7,L		
0	152	-157
1	264	265
2	152	-150
3	193	-193
4	17	-8
5	24	-22
6	34	31
6,8,L		
0	129	-121
1	132	-104
2	8	4
3	135	132
4	25	-21
7,0,L		
2	1409	1394E
4	925	-917
6	735	705
8	4*	7
10	93	-111
7,1,L		
1	650	627
2	120	123
3	223	-223
4	38	-45
5	87	87
6	291	290
7	136	-140
8	69	-68
9	71	-72
10	16*	-34
7,2,L		
1	169	172
2	596	-601
3	150	-137
4	614	609
5	198	-196
6	559	-548
7	78	77
8	85	84
9	55	-51
10	164	167
7,3,L		
1	559	-559
2	213	-219
3	91	85
4	510	517
5	224	-229
6	11	-3
7	162	163
8	44	-45
9	56	54
7,4,L		
1	132	97
2	138	130
3	401	-417
4	344	-343
5	228	228
6	195	186
7	27	-21
9	4*	-3
7,5,L		
1	37	-37
2	90	90
3	67	68
4	220	-219
5	218	219
6	118	113
7	27	24
8	16	-3
7,6,L		
1	56	-52
2	190	-139
3	431	437
4	342	337
5	255	-251
6	32	-33
7	99	89
7,7,L		
1	97	-97
2	86	-84
3	58	53
4	92	-91
5	103	-104
6	158	-152
7,8,L		
1	18	18
2	54	56
3	215	-220
8,0,L		
0	57	-62
2	439	442
4	468	448
6	324	-315
8	510	517
10	192	-132
8,1,L		
0	22	9
1	221	215
2	100	100
3	149	134
4	52	-51
5	69	-60
6	166	162
7	107	-134
8	169	169
9	26	22
10	33	22
8,2,L		
0	122	124
1	479	465
2	353	-339
3	26	-16
4	106	-95
5	291	295
6	91	85
7	13	-17
8	351	-351
9	136	145
8,3,L		
0	12	-21
1	9	-10
2	106	-84
3	47	60
4	194	-236
5	48	26
6	87	92
7	120	120
8	90	82
9	26	26
8,4,L		
0	205	-199
1	226	226
2	236	234
3	180	-172
4	101	-133
5	207	-239
6	100	132
7	89	89
8	95	93
8,5,L		
0	179	192
1	112	-116
2	45	-46
3	237	-249
4	8*	9
5	42	-34
6	16	-20
7	25	22
8	15	-12
8,6,L		
0	39	45
1	511	-521
2	122	-118
3	289	287
4	17	-15
5	32	32
6	36	38
7	163	-161
8,7,L		
0	43	-42
1	81	-78
2	5*	0
3	17	-12
4	26	20
5	83	80
8,8,L		
0	104	131
1	302	336
2	8	15
3	159	-154
9,0,L		
2	472	-459
4	845	831
6	494	-496
8	175	178
9,1,L		
1	301	-298
2	199	-198
3	92	-100
4	392	-380
5	279	273
6	235	-231
7	59	-58
8	39	-34
9	83	81
9,2,L		
1	149	144
2	539	542
3	292	-289
4	699	-696
5	229	235
6	408	407
7	61	-63
8	67	-69
9	17	14
9,3,L		
1	43	-53
2	85	-81
3	182	181
4	78	-82
5	279	-282
6	282	-283
7	59	59
8	8*	-1
9	44	-41
9,4,L		
1	149	-154
2	443	-442
3	182	175
4	399	399
5	253	-254
6	290	-291
7	133	131
8	8	-11
9,5,L		
1	415	434
2	271	273
3	45	44
4	26	25
5	20	5
6	169	167
7	34	-35
9,6,L		
1	178	182
2	139	137
3	175	-173
4	183	-184
5	250	247
6	186	176
9,7,L		
1	113	-117
2	44	-41
3	150	-144
4	49	46
5	65	-67
9,8,L		
1	137	-139
2	49	-52
10,0,L		
0	87	83
2	237	227
4	363	362
6	59	47
8	22	-18
10,1,L		
0	34	-30
1	283	-276
2	306	308
3	119	-116
4	194	191
5	137	-139
6	322	-310
7	97	98
8	205	200
9	65	-63
10,2,L		
0	312	-305
1	656	669
2	73	67
3	105	99
4	78	-75
5	91	93
6	239	-238
7	266	267
8	25	21
9	25	-23
10,3,L		
0	410	412
1	25	27
2	284	-297
3	46	49
4	148	149
5	186	190
6	64	-70
7	160	-165
8	282	-275
9	113	115
10,4,L		
0	282	277
1	249	-251
2	200	-204
3	70	71
4	71	-78
5	143	-145
6	243	243
7	215	-210
8	90	-93
10,5,L		
0	370	-383
1	377	387
2	271	282
3	24	5
4	43	-42
5	26	16
6	12	17
7	102	105
10,6,L		
0	30	-25
1	104	102
2	38	-41
3	70	-78
4	59	-52
5	30	-28
6	13	-12
10,7,L		
0	7*	-5
1	198	-199
2	113	-119
3	131	128
4	71	-67
10,8,L		
0	44	48
1	186	-190
11,0,L		
2	12	-22
4	306	-299
6	191	194
8	126	-125
11,1,L		
1	213	207
2	465	-450
3	53	59
4	492	487
5	71	-67
6	360	-348
7	24	-21
8	31	28
9	69	-67
11,2,L		
1	143	-135
2	317	-317
3	321	325
4	426	424
5	12	-8
6	148	-151
7	15	-11
8	53	49
9	65	69
11,3,L		
1	162	-163
2	224	214
3	224	-232
4	109	-105
5	129	133
6	171	169
7	31	-28
8	32	-31
11,4,L		
1	69	-73
2	352	366
3	110	-106
4	344	-345
5	126	129
6	199	198
7	126	-125
8	26	-21
11,5,L		
1	50	-47
2	59	-61
3	356	373
4	122	119
5	162	-159
6	12	-16
7	149	145
11,6,L		
1	16	-15
2	63	-66
3	107	102
4	94	91
5	116	-120
6	207	-203
11,7,L		
1	38	37
2	6*	-2
3	296	-301
4	196	-199
12,0,L		
0	36	-35
2	103	103
4	184	-190
6	265	262
8	116	115
12,1,L		
0	611	617
1	8*	-4
2	570	-569
3	222	221
4	180	191
5	186	186
6	320	304
7	85	82
8	271	-270
9	28	-20
12,2,L		
0	90	-100
1	222	-222
2	13	4
3	47	46
4	112	-111
5	33	-37
6	102	-97
7	152	152
8	13	-4
12,3,L		
0	693	-726
1	98	102
2	95	75
3	276	-280
4	57	-41
5	170	-166
6	177	-170
7	34	-25
8	287	286
12,4,L		
0	323	327
1	51	-56
2	134	-135
3	148	-154
4	215	219
5	11	2
6	12	-19
7	45	-47
12,5,L		
0	272	278
1	269	-280
2	21	15
3	82	79
4	48	46
5	23	-17
6	121	119
12,6,L		
0	226	-229
1	43	45
2	34	27
3	40	45
4	20	9
5	121	115
12,7,L		
0	29	29
1	298	305
2	133	132
3	47	-49
13,0,L		
2	233	-240
4	176	-170
6	278	-273
8	58	-67
13,1,L		
1	115	121
2	99	89
3	159	-156
4	383	-372
5	115	115
6	213	219
7	92	89
8	12	13
13,2,L		
1	136	144
2	116	117
3	174	180
4	12	-7
5	186	-176
6	57	54
7	84	82
8	30	30
13,3,L		
1	210	-210
2	435	-438
3	116	113
4	318	321
5	251	-262
6	193	-193
7	17	15
13,4,L		
1	134	111
2	84	80
3	114	-113
4	97	102
5	20	17
6	114	114
7	83	-84
13,5,L		
1	193	197
2	159	164
3	43	-43
4	164	-161
5	244	241
6	157	152
13,6,L		
1	96	-101
2	71	-66
3	35	-36
4	12	-11
13,7,L		
1	157	-159
2	48	39
14,0,L		
0	457	-457
2	448	442
4	49	-43
6	141	-138
8	228	221
14,1,L		
0	112	-103
1	338	342
2	480	494
3	95	-95
4	137	-111
5	58	-58
6	71	-65
7	48	48
8	134	136
14,2,L		
0	392	393
1	112	-114
2	318	-321
3	142	144
4	17	-8
5	11	11
6	99	96
7	29	-33
14,3,L		
0	407	412
1	375	-375
2	288	-295
3	126	131
4	175	-177
5	31	-31
6	156	184
7	123	-127
14,4,L		
0	203	-204
1	186	196
2	194	198
3	74	-80
4	76	69
5	36	-28
6	81	-72
14,5,L		
0	194	-192
1	75	72
2	112	112
3	7*	3
4	38	41
5	63	59
14,6,L		
0	71	71
1	136	-142
2	154	-153
3	39	45
4	35	-31
15,0,L		
2	113	-105
4	295	291
6	212	-202
15,1,L		
1	54	57
2	53	54
3	173	176
4	201	203
5	10	-6
6	13	-10
7	80	-74
15,2,L		
1	137	-139
2	214	211
3	118	-121
4	149	-145
5	43	31
6	170	166
7	133	129
15,3,L		
1	97	-93
2	254	256
3	207	-208
4	93	-96
5	59	56
6	89	87
7	20	-24
15,4,L		
1	14	9
2	148	-146
3	135	137
4	14	8
5	164	-160
6	98	-101
15,5,L		
1	20	-20
2	98	-100
3	93	86
4	37	42
5	94	-97
15,6,L		
1	145	142
2	45	-39
3	177	-181
16,0,L		
0	511	510
2	528	-534
4	262	267
6	264	257
16,1,L		
0	275	275
1	56	55
2	81	76
3	38	-37
4	106	106
5	59	54
6	124	122
7	9	-1
16,2,L		
0	639	-640
1	183	186
2	288	286
3	220	-224
4	64	-63
5	144	-142
6	245	-244
16,3,L		
0	188	-188
1	78	-79
2	18	-14
3	14	10
4	32	-27
5	63	-61
6	12	-12
16,4,L		
0	422	433
1	139	-145
2	44	-28
3	111	108
4	60	-50
5	20	-13
16,5,L		
0	23	10
1	34	-27
2	68	-68
3	71	72
4	46	41
16,6,L		
0	34	-36
1	190	198
17,0,L		
2	58	-60
4	236	-235
6	111	117
17,1,L		
1	38	-37
2	9*	0
3	42	44
4	77	75
5	11	-11
6	13	1
17,2,L		
1	124	-125
2	179	-182
3	180	178
4	246	249
5	111	-114
6	92	-98
17,3,L		
1	55	50
2	78	76
3	60	-60
4	146	-144
5	26	23
17,4,L		
1	86	87
2	222	224
3	88	-87
4	175	-178
17,5,L		
1	9	-5
2	81	-73
3	37	36
18,0,L		
0	81	72
2	367	372
4	33	28
6	184	-182
18,1,L		
0	340	338
1	115	-120
2	44	-41
3	22	20
4	133	130
5	17	-16
18,2,L		
0	260	266
1	133	-134
2	305	-309
3	69	70
4	55	-55
5	182	179
18,3,L		
0	138	-136
1	139	141
2	16	10
3	83	-83
4	47	40
18,4,L		
0	454	-459
1	127	128
2	187	184
3	35	-37
18,5,L		
0	13	-5
19,0,L		
2	15	15
4	154	159
19,1,L		
1	28	-17
2	185	186
3	80	-80
4	256	-252
5	21	-17
19,2,L		
1	43	-47
2	76	78
3	101	-100
4	35	-41
19,3,L		
1	49	44
2	239	-238
3	96	98
19,4,L		
1	65	-61
20,0,L		
0	236	230
2	8	-1
4	17	15
20,1,L		
0	146	-149
1	59	62
2	190	193
3	26	19
20,2,L		
0	198	-197
1	118	-116
2	17	16
3	8	-5
20,3,L		
0	250	251
1	80	-85
21,0,L		
2	56	-55
21,1,L		
1	63	-62

schungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr W. R. Busing for sending a preprint of the neutron diffraction work.

References

Altenburg, H. & Mootz, D. (1971). *Acta Cryst.* **B27**, 1982.

Busing, W. R. & Kostansek, E. C. (1971). ACA. Winter Meeting in Columbia, S.C., Abstract *F*2, p. 35.

Cole, F. E. (1966). Dissertation, Washington State Unisity.

Dickens, B. & Bowen, J. S. (1971). *Acta Cryst.* **B27**, 2247.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040.

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

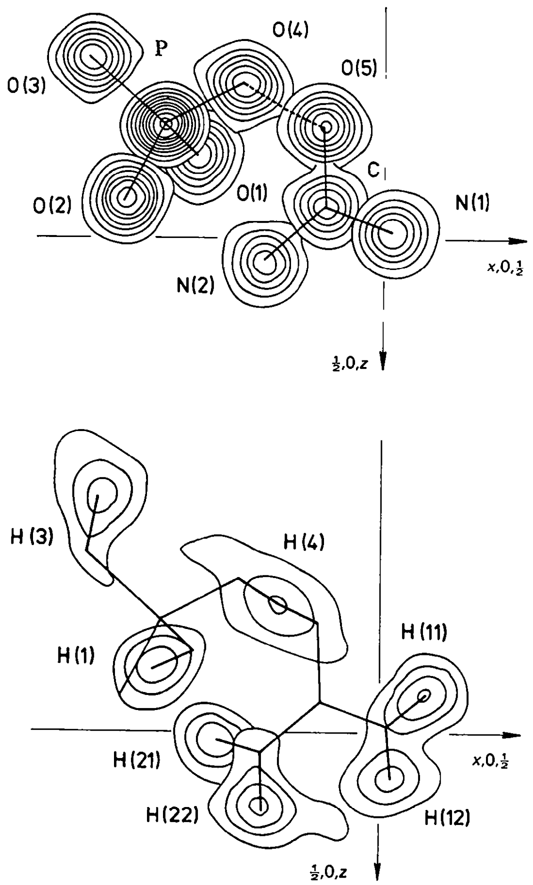

Fig. 1. Fourier and difference Fourier synthesis. The starting line corresponds to 1 e.Å^{-3} for P, O, N, C and 0·1 e.Å^{-3} for H. The increment is 4 e.Å^{-3} for P, 2 e.Å^{-3} for O, N, C and 0·2 e.Å^{-3} for H.

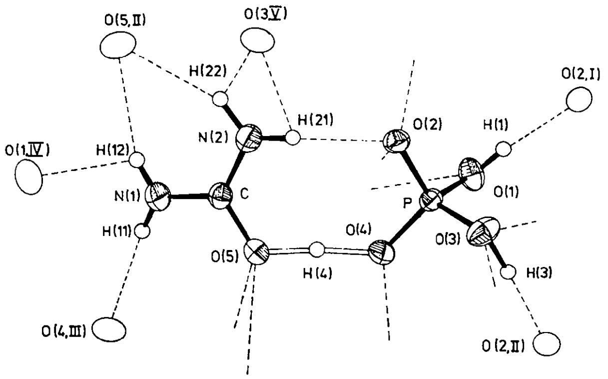

Fig. 2. The asymmetric unit with hydrogen bonds. The proton donor group O–H or N–H is omitted for simplicity where it does not belong to the basic unit.

Table 3. *Lengths and angles of covalent bonds*

Acid moiety		Base moiety	
P-O(1)	1·557 (2) Å	C-N(1)	1·319 (3) Å
P-O(2)	1·508 (1)	C-N(2)	1·324 (3)
P-O(3)	1·554 (2)	C-O(5)	1·278 (3)
P-O(4)	1·516 (2)		
		N(1)—H(11)	0·79 (3) Å
O(1)—H(1)	0·82 (3) Å	N(1)—H(12)	0·82 (3)
O(3)—H(3)	0·93 (3)	N(2)—H(21)	0·88 (3)
O(4)···H(4)	1·25 (4)	N(2)—H(22)	0·91 (3)
		O(5)···H(4)	1·18 (4)
O(1)-P-O(2)	112·1 (1)°	N(1)-C-N(2)	120·1 (2)°
O(1)-P-O(3)	108·4 (1)	N(1)-C-O(5)	119·1 (2)
O(1)-P-O(4)	104·7 (1)	N(2)-C-O(5)	120·9 (2)
O(2)-P-O(3)	106·9 (1)		
O(2)-P-O(4)	113·8 (1)	C-N(1)—H(11)	119 (2)°
O(3)-P-O(4)	111·0 (1)	C-N(1)—H(12)	118 (1)
		C-N(2)—H(21)	119 (2)
P-O(1)—H(1)	112 (2)°	C-N(2)—H(22)	117 (2)
P-O(3)—H(3)	122 (2)	C-O(5)···H(4)	118 (1)
P-O(4)···H(4)	126 (2)		
		H(11)-N(1)-H(12)	122 (3)°
		H(21)-N(2)-H(22)	124 (3)

Table 4. *Geometry of hydrogen bonds*

X–H···O	d(X···O)	d(X–H)	d(H···O)	angle at H
O(1)—H(1)···O(2,I)	2·667 (2) Å	0·82 (3) Å	1·85 (3) Å	173 (3)°
O(3)—H(3)···O(2,II)	2·591 (2)	0·93 (3)	1·67 (3)	177 (3)
O(4)···H(4)···O(5)	2·424 (2)	1·25 (4)	1·18 (4)	173 (4)
N(1)–H(11)···O(4,III)	2·935 (3)	0·79 (3)	2·15 (3)	175 (3)
N(1)–H(12)···O(5,II)	3·130 (3)	0·82 (3)	2·40 (3)	149 (3)
N(1)–H(12)···O(1,IV)	3·160 (3)	0·82 (3)	2·81 (3)	108 (2)*
N(2)–H(21)···O(2)	2·979 (3)	0·88 (3)	2·10 (3)	177 (3)
N(2)–H(21)···O(3,V)	2·995 (3)	0·88 (3)	2·87 (3)	89 (3)*
N(2)–H(22)···O(3,V)	2·995 (3)	0·91 (3)	2·70 (2)	100 (3)*
N(2)–H(22)···O(5,II)	3·099 (3)	0·91 (3)	2·40 (3)	154 (3)

I: $\frac{1}{2}-x,\ \frac{1}{2}+y,\ z$
II: $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$
III: $-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$
IV: $-x,\ -y,\ -z$
V: $\frac{1}{2}-x,\ -y,\ \frac{1}{2}+z$

In view of their large d(H...O) and small angles at the proton the interactions marked* should probably not be considered as 'normal' hydrogen bonds.

KOSTANSEK, E. C. & BUSING, W. R. (1972). *Acta Cryst.* **B28**, 2454.
MOOTZ, D. & ALTENBURG, H. (1971). *Acta Cryst.* **B27**, 1520.
PRYOR, A. W. & SANGER, P. L. (1970). *Acta Cryst.* **A26**, 543.
STEWART, J. M. & HIGH, D. (1965). X-ray 63, Program System for X-ray Crystallography. The Departments of Chemistry at the Univ. of Washington, Seattle, and the Univ. of Maryland, College Park.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
SUNDERA-RAO, R. V. G., TURLEY, J. W. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 435.
WOLFRAM, W., ARUTUNIAN, E. G., ANTISHKINA, A. S. & PORAI-KOSHITS, M. A. (1967). *Bull. Acad. Pol. Sci. Sér. Sci. chim.* **15**, 83.
WORSHAM, J. E. & BUSING, W. R. (1969). *Acta Cryst.* **B25**, 572.

Acta Cryst. (1972). **B28**, 2463

The Crystal Structure of 3,4-Epoxysulfolane

BY DONALD E. SANDS

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, *U.S.A.*

(*Received* 14 *January* 1972)

The compound 3,4-epoxysulfolane, $C_4H_6OSO_2$, crystallizes in the orthorhombic system with four molecules in a unit cell of symmetry $P2_12_12_1$ and dimensions $a=8{\cdot}475$ (6), $b=10{\cdot}742$ (5), $c=5{\cdot}899$ (4) Å. Least-squares refinement of 1282 observed structure factors, measured on a Pailred diffractometer, gave a residual of 0·055. The molecule is folded so that the epoxide linkage is nearly normal to the mean plane of the sulfur and carbon atoms. Analysis of the thermal motion by the rigid-body method of Schomaker and Trueblood shows that the least librational oscillation is about the normal to the sulfur–carbon mean plane.

Introduction

Compounds with the formula SO_2X_2 may be sulfuryl halides, such as SO_2F_2, or symmetrically substituted sulfones, such as dimethyl sulfone, $(CH_3)_2SO_2$. The sulfur atom in these molecules is tetrahedrally coordinated, and the simplest prototypes have C_{2v} symmetry. We have previously determined the structures of dimethyl sulfone (Sands, 1963) and butadiene sulfone, $C_4H_6SO_2$ (preferred name is 2,5-dihydrothiophene-1,1-dioxide, also known as 3-sulfolene) (Sands & Day, 1967). The present paper reports the structure of 3,4-epoxysulfolane, $C_4H_6OSO_2$ (alternative names are butadiene sulfone epoxide and sulfolene-3-epoxide).

Experimental

The epoxidation of butadiene sulfone was accomplished by treatment with performic acid, as described by Sorenson (1959). The product was recrystallized from acetone and it melted in the range 123–125 °C. A preparation by another method by van Lohuizen & Backer (1949) was reported to melt at 130 °C, and Procházka & Horák (1959) observed a melting point in the range 124·5–126°. Sorenson (1959), however, observed a melting point of 159–160° and suggested the possible existence of two crystalline modifications, although he was unable to convert his product into a second crystalline form. Subsequently, Loev (1961) reported the