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The Crystal and Molecular Structure of 4-(2',4'-Dinitrobenzyl)pyridine

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The crystal and molecular structure of 4-(2',4'-dinitrobenzyl)pyridine has been determined crystallographically from the 2300 unique and significant reflections for which $2\theta < 60°$, and refined to an R index of 0·056. Counter methods with graphite monochromated Mo $K\alpha$ radiation were employed. All hydrogen atoms were included in the least-squares refinement. Crystals form in the monoclinic space group $P2_1/c$ with cell dimensions $a = 7·214$ (2), $b = 13·344$ (5), $c = 12·553$ (5) Å and $\beta = 102·56$ (3)°. Estimated standard deviations in non-hydrogen bond lengths range from 0·002 to 0·003 Å and, in angles, from 0·14 to 0·21°. The intramolecular angle between the planes of the two aromatic rings is 70·7°. The closest approach of a methylene hydrogen atom to an electronegative atom is intramolecular to an oxygen atom (at 2·5 Å) on the *o*-nitro group. This nitro group is rotated 38·5° from the plane of the benzyl ring; the other is twisted 8·5° from the benzyl plane. No short intermolecular contacts involving the methylene hydrogen atoms were found.

Introduction

When the pale-yellow crystals of 2-(2',4'-dinitrobenzyl)pyridine (α-DNBP) are irradiated with light of wavelength 4000 Å or less, a deep blue substance is produced by a reversible tautomeric reaction (Hardwick, Mosher & Passalaigue, 1960). The half-life of the excited form is several hours in the crystal, but only a few seconds or less in various solvents. The related compound 4-(2',4'-dinitrobenzyl)pyridine (γ-DNBP), does not show this high solid-state tautomeric stability (Mosher, Hardwick & Ben-Hur, 1962).

In both α-DNBP and γ-DNBP the methylene hydrogens are the most acidic (Bowden & Stewart, 1965), and therefore are the most likely to be involved in the tautomerization reaction. A short intramolecular contact of 2·4 Å involving one of the methylene hydrogens and an oxygen of the *o*-nitro group was found in the crystal structure of α-DNBP (Seff & Trueblood, 1968). An intramolecular transfer of this hydrogen to the *o*-nitro group was suggested as the first step in the tautomerization reaction: this would leave the two rings interconjugated and would shift the absorption maximum to longer wavelengths. The hydrogen atom might then be transferred intramolecularly to the pyridine nitrogen atom. The distance between the oxygen atom and the pyridine nitrogen atom was found to be 3·3 Å. A short intermolecular contact between the other methylene hydrogen and one of the oxygens on the *p*-nitro group was also found.

The structure determination of γ-DNBP was carried out to find the difference between the molecular and crystal structures of α-DNBP and γ-DNBP. This may help in establishing the reaction scheme for the tautomerization, and explain the different behavior of the two closely related compounds.

Experimental

Crystals of γ-DNBP form in the monoclinic space group $P2_1/c$ (Seff & Trueblood, 1968). Crystals were supplied by R. Hardwick and D. Ben-Hur.

A Syntex $P\bar{1}$ four-circle computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($K\alpha_1$, $\lambda = 0·70926$ Å; $K\alpha_2$, $\lambda = 0·71354$ Å) and pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 26·0°. The program used was written by R. E. Sparks and is part of the diffractometer program library. The temperature was maintained within 1° of 20°C.

A crystal of dimensions $0·65 \times 0·5 \times 0·5$ mm was used for data collection. The θ–2θ scanning mode was utilized with scan speed variable from 2 to 24° min^{-1}, depending on the peak intensity of the reflection. Background counting time was equal to scan time, and the scan range varied from 2·0° at low 2θ to 2·4° at 60°. The variations in the intensities of three check reflections, which were remeasured after every 100 during data collection, were all less than two times their standard deviations, so no decay correction was applied.

Standard deviations were assigned to the individual reflections according to the formula,

$$\sigma(I) = [\omega^2(CT + B_1 + B_2) + (pI)^2]^{1/2},$$

where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega[CT - (B_1 + B_2)]$. A value of 0·02 was assigned to the empirical parameter p to account for instrument instability. The weights, w, used in the least-squares procedure were the reciprocal squares of $\sigma(F_o)$. Of the 3462 reflections measured, those for which $2\theta < 60°$, 2300 had intensities larger than three times their

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Table 1. *Observed and calculated structure factors*

The running index is l; values of h and k for each group immediately precede that group. The central column is $10|F_o|$; the right-hand column is $10F_c$. All of the X-ray diffraction intensities which were observed to be greater than three times their standard deviations were used in structure refinement and are listed in this table.

H=	0, K=	0
4	152	147
6	87	-84
8	114	109
10	95	91
14	32	-27
H=	0, K=	1
1	170	155
2	265	-249
3	188	183
4	22	25
5	167	-147
6	61	52
7	201	-200
8	13	-10
9	78	73
10	64	-62
11	43	-40
12	117	118
14	37	37
H=	0, K=	2
0	154	149
3	123	127
4	51	44
5	189	178
6	40	40
7	60	-61
8	237	-225
9	165	-157
11	126	119
14	48	-45
15	37	-39
16	24	-19
17	26	-25
H=	0, K=	3
1	40	-34
2	394	357
4	23	20
5	532	499
7	19	-11
8	161	160
9	28	-30
10	86	-91
11	17	-22
12	71	76
13	60	-58
14	54	-56
15	20	-14
17	20	23
H=	0, K=	4
0	222	-222
1	30	28
2	340	330
3	515	474
4	148	143
5	186	-158
6	143	135
7	148	149
8	106	102
9	77	-70
10	92	-89
11	147	138
12	29	33
13	39	-44
15	47	43
H=	0, K=	5
1	119	105
2	233	203
3	347	-313
5	229	-212
6	114	113
8	195	195
9	17	-15
10	156	-155
11	28	30
12	26	21
14	23	-29
H=	0, K=	6
0	220	-204
1	122	-120
2	321	285
3	135	128
4	44	55
5	187	177
6	61	-60
7	42	42
9	19	-15
10	170	-161
11	18	14
12	45	49
14	21	18
H=	0, K=	7
1	16	16
2	190	167
3	33	33
4	44	-33
5	24	19
6	17	-13
8	107	107
9	36	-34
12	76	73
H=	0, K=	8
0	510	-466
1	224	-199
3	86	-92
4	53	-46
5	108	104
6	131	129
7	104	100
8	45	54
10	24	24
13	21	-14
14	24	21
15	22	-19
H=	0, K=	9
1	59	-43
3	47	43
4	36	31
5	40	31
6	72	67
8	81	81
9	95	96
10	17	-15
11	26	-22
12	56	-63
H=	0, K=	10
0	17	16
1	72	-65
3	24	-23
4	65	-65
6	89	-92
7	123	125
9	32	-31
10	37	35
11	22	27
12	19	-20
H=	0, K=	11
1	29	-10
2	104	110
3	81	-79
4	20	14
5	86	-84
6	86	-63
7	79	-57
8	27	-26
9	63	61
10	65	62
12	30	-30
13	37	38
H=	0, K=	12
0	110	107
1	51	48
2	57	50
3	90	90
4	59	-59
5	31	-30
8	52	53
9	24	-27
10	26	27
11	42	41
H=	0, K=	13
2	26	-23
6	25	32
7	40	41
8	39	-36
10	24	18
11	35	-33
H=	0, K=	14
0	185	-194
1	105	-107
2	52	-49
4	20	-24
7	20	-26
8	22	-26
H=	0, K=	15
1	64	-67
3	49	51
7	42	42
9	28	-27
H=	0, K=	16
1	23	-30
2	57	56
3	48	53
7	55	-56
8	29	-21
9	51	51
H=	0, K=	17
3	29	-24
5	49	-48
6	33	-35
7	27	25
H=	0, K=	18
1	27	-26
3	26	-25
4	20	-17
5	28	29
H=	1, K=	0
-16	44	-51
-14	98	100
-12	42	-44
-10	54	44
-8	28	25
-6	152	151
0	296	-281
4	149	142
6	129	122
8	68	-63
10	30	31
12	144	145
14	62	64
H=	1, K=	1
-15	38	35
-14	48	-46
-12	110	106
-11	19	17
-10	101	-103
-8	225	-216
-7	118	-114
-6	196	-187
-5	92	106
-4	295	-285
3	17	-6
4	252	-247
5	395	-367
6	213	-200
7	284	259
8	137	140
9	202	-201
10	103	98
11	38	-34
12	21	-21
14	77	-75
15	18	12
H=	1, K=	2
-16	33	-35
-15	23	-29
-14	72	68
-12	93	-94
-11	23	27
-10	15	8
-9	60	-64
-8	64	63
-7	84	74
-6	294	280
-5	97	-84
-2	27	-27
-1	399	-379
0	228	-216
1	355	326
2	187	171
3	14	11
4	493	-463
5	88	-82
6	199	-192
7	23	-20
8	131	-125
9	88	88
10	22	-23
11	21	-21
12	99	-97
13	29	-32
14	24	-22
15	26	-30
16	21	-19
H=	1, K=	3
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-14	103	-104
-13	49	-54
-12	127	121
-11	62	60
-10	18	-29
-9	70	65
-8	29	32
-7	224	225
-6	187	177
-5	12	-5
-4	510	-462
-3	83	-93
1	473	442
3	40	-44
4	188	-174
5	275	-255
6	70	63
8	71	63
9	119	124
12	46	-47
15	45	47
H=	1, K=	4
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-12	68	67
-11	80	-77
-10	36	40
-9	14	4
-8	75	71
-7	35	29
-6	176	168
-5	464	-416
-4	34	-41
-3	25	21
-2	464	428
-1	409	-373
0	117	-105
1	121	-120
2	67	63
3	257	251
4	114	107
6	22	-21
7	44	-48
9	59	-58
11	76	-75
13	22	24
14	49	49
15	26	29
16	30	-34
H=	1, K=	5
-14	24	-24
-13	28	-23
-12	66	60
-11	39	34
-10	95	-101
-8	32	27
-7	95	-81
-6	269	252
-5	100	85
-4	258	-218
-3	66	-68
-2	238	225
-1	122	120
0	342	323
1	17	-15
2	383	360
3	22	21
4	69	-60
5	53	-48
6	42	-35
7	187	-194
8	97	-93
10	55	-61
11	31	-35
12	24	-21
15	23	-23
H=	1, K=	6
-16	25	27
-14	49	-50
-12	17	-19
-11	16	-21
-10	48	-48
-9	41	-38
-8	26	21
-7	144	136
-6	169	-164
-5	15	28
-4	23	-14
-3	403	366
-2	69	64
-1	260	252
0	80	72
1	188	174
2	426	-396
3	24	-23
4	138	-135
5	180	179
6	40	37
7	266	-256
9	115	111
10	31	34
11	63	-68
12	34	37
13	22	-20
H=	1, K=	7
-14	20	-20
-13	19	-17
-10	39	-38
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-8	46	-45
-7	87	77
-6	88	-85
-5	62	-67
-4	204	193
-3	251	-228
-2	125	-117
-1	198	178
1	116	119
2	154	-136
3	54	59
4	49	44
5	56	-48
6	61	-51
7	135	-144
8	59	62
9	123	119
H=	1, K=	8
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-12	51	51
-10	41	42
-9	17	16
-8	18	-22
-5	53	52
-4	29	38
-3	94	93
-2	103	-96
-1	158	151
0	164	150
2	216	200
5	190	186
6	192	191
7	196	-195
8	115	-120
9	82	88
13	20	-19
14	37	-37
H=	1, K=	9
-15	33	-32
-13	27	27
-12	31	-25
-10	55	-55
-9	34	-38
-8	38	33
-6	131	135
-4	187	174
-3	79	-68
-2	176	-165
-1	32	-38
0	70	60
1	34	-35
2	198	193
3	110	118
4	176	179
5	116	116
6	105	-106
7	26	-13
8	81	-81
9	31	31
10	70	-72
12	20	-18
14	38	39
H=	1, K=	10
-12	25	19
-10	61	-66
-8	30	-50
-7	20	25
-5	71	-77
-4	77	62
-3	158	-149
-2	175	-163
-1	30	-27
1	29	24
2	52	-54
3	14	17
4	58	-59
5	31	37
6	91	88
7	62	-61
9	36	-38
14	30	-32
H=	1, K=	11
-11	28	-25
-9	27	-29
-8	49	48
-7	85	-91
-6	36	-36
-5	50	58
-3	29	25
-1	103	102
0	96	96
1	85	-83
3	44	-50
4	37	-37
5	91	89
6	72	77
7	47	46
8	65	67
9	43	-41
10	36	-37
13	39	-38
H=	1, K=	12
-13	33	-30
-11	42	39
-10	17	-22
-5	38	-43
-4	23	20
-3	173	175
-2	68	72
-1	111	117
0	38	41
3	59	-64
4	112	115
5	32	-32
6	18	13
7	64	62
8	40	44
12	42	41
H=	1, K=	13
-11	23	26
-8	36	-35
-7	35	-35
-6	52	-56
-5	21	24
-4	45	48
-3	47	-48
-2	40	-38
-1	24	27
0	54	-55
3	35	-34
4	119	-123
5	49	51
9	20	-20
10	23	23
11	36	36
H=	1, K=	14
-11	31	30
-9	30	-30
-4	80	-84
-3	21	21
-2	59	-57
-1	82	-85
0	28	26
1	33	-34
3	69	69
4	77	76
5	20	-20
6	115	-113
8	36	36
10	24	-22
11	38	38
H=	1, K=	15
-10	24	27
-7	20	16
-4	36	37
-3	62	-65
0	58	57
1	73	72
2	62	62
4	37	-36
6	59	59
7	31	25
8	26	-28
H=	1, K=	16
-9	22	24
-5	28	-34
-4	41	46
-3	25	-26
0	23	29
2	24	-27
3	21	-16
4	52	54
6	43	-42
8	49	49
H=	1, K=	17
-5	22	-23
-4	27	-25
-3	28	31
-2	48	-53
0	26	25
2	24	-31
4	33	-33
6	26	32
H=	1, K=	18
-5	48	45
-4	23	20
H=	2, K=	0
-16	60	59
-14	37	-36
-10	117	-110
-8	65	63
-6	126	-116
-4	358	-343
0	78	-59
2	428	413
4	381	337
6	312	-284
8	67	63
10	146	147
12	120	118
14	59	-66
H=	2, K=	1
-17	65	68
-16	26	25
-15	91	-87
-14	34	-30
-13	48	44
-12	45	-46
-11	56	56
-10	136	-136
-9	47	-37
-8	63	63
-7	188	191
-6	234	225
-5	175	-183
-4	42	-39
-3	228	-214
-1	80	73
0	43	44
1	57	61
2	548	-516
4	104	113
5	115	-130
6	204	-193
8	26	-27
9	94	91
10	147	-147
11	77	80
12	112	-115
13	28	-30
15	24	25
H=	2, K=	2
-14	21	-27
-12	20	28
-11	69	-65
-10	27	35
-9	28	24
-8	40	36
-7	16	25
-5	541	514
-4	106	-109
-3	24	-26
-2	100	87
0	345	-323
1	248	-246
2	388	-366
3	111	-94
4	237	213
5	302	278
6	58	59
7	148	142
8	26	-30
9	24	25
10	62	-63
11	40	-38
12	47	49
13	56	58
15	24	19
H=	2, K=	3
-16	19	16
-13	19	14
-12	43	42
-10	23	14
-9	106	-101
-7	187	-187
-6	444	419
-5	218	-203
-4	116	-116
-3	315	-292
-2	113	-112
-1	416	-394
0	103	102
2	16	18
3	397	-373
4	156	141
5	350	320
6	106	-109
7	131	129
8	24	-25
9	21	17
10	95	94
11	40	-40
12	65	61
14	27	30
15	28	27
H=	2, K=	4
-14	38	42
-10	25	-23
-9	134	133
-7	439	-408
-6	53	55
-5	331	307
-4	174	-168
-3	31	29
-2	123	118
-1	173	145
0	351	322
1	128	-124
2	409	-384
3	237	-224
4	218	197
5	82	-87
6	25	27
7	166	-169
8	118	121
9	151	-153
10	37	34
H=	2, K=	5
-17	20	-17
-15	19	17
-14	18	-11
-12	36	-37
-11	24	-22
-10	75	74
-9	123	122
-7	165	-157
-6	87	-93
-5	620	591
-4	326	-339
-3	149	-150
-2	194	157
0	95	-92
1	47	44
3	138	127
4	359	-336
5	144	-143
8	72	-77
12	65	63
H=	2, K=	6
-16	29	-29
-13	26	-31
-11	29	26
-10	22	-23
-9	125	128
-8	167	-161
-7	63	-63
-6	251	-242
-5	248	234
-3	108	-103
-2	43	-35
-1	125	-117
0	62	-61
1	97	-91
2	414	-381
3	219	-199
4	87	69
5	41	41
6	46	-47
7	35	34
9	16	8
10	44	42
11	65	69
12	18	-18
13	24	-28
14	28	-21
15	36	37
H=	2, K=	7
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-14	42	40
-10	25	-26
-8	65	59
-7	203	-191
-6	136	143
-5	143	141
-4	203	205
-3	88	84
-2	123	-122
-1	100	-92
0	147	-140
1	149	-148
2	60	56
3	183	172
4	197	-200
5	60	-57
6	91	89
7	74	77
8	15	-21
10	81	-80
11	60	-64
12	26	33
13	53	51
14	54	-52
H=	2, K=	8
-14	30	31
-10	28	22
-9	29	27
-8	104	111
-6	90	89
-5	75	70
-4	136	136
-3	98	-97
-2	195	190
0	170	153
2	59	54
4	104	-108
5	179	-185
6	93	94
7	57	54
8	27	-32
11	73	71
13	72	-74
H=	2, K=	9
-15	27	29
-13	29	-28
-11	42	-40
-10	96	96
-8	60	-57
-7	99	99
-6	58	-49
-5	174	-173
-4	110	-114
-3	15	-20
-2	87	80
-1	20	-30
0	41	42
1	42	35
2	108	-106
3	47	53
4	250	-250
5	135	-129
6	83	75
7	39	40
11	72	-74
12	40	41
13	43	46
H=	2, K=	10
-11	27	24
-10	37	-45
-9	57	57
-8	52	51
-7	34	-38
-6	69	-71
-5	162	-163
-4	61	-57
-3	94	90
-2	71	-62
-1	139	137
0	57	-57
1	54	-55
2	181	178
3	79	84
4	106	-99
5	205	-212
7	37	-41
8	67	-72
9	45	-45
11	28	26
12	30	29
13	23	-31
H=	2, K=	11
-13	19	-23
-11	28	26
-10	22	22
-9	26	25
-8	65	-68
-7	84	83
-6	90	93
-4	26	24
-3	147	146
-1	43	42
0	72	64
1	74	73
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H=	5, K=	13
-8	22	-20
-5	18	19
-4	51	-52
-3	21	20
-2	31	-32
-1	31	33
2	25	28
3	49	46
4	34	37
5	31	28
6	41	-40
H=	5, K=	14
-5	38	38
1	36	36
2	21	-22
5	30	24
H=	5, K=	15
-6	19	16
-5	51	55
-3	60	-60
-2	22	25
-1	38	40
2	34	-30
4	29	24
H=	5, K=	16
-5	21	21
-3	25	-26
0	20	13
1	23	21
H=	6, K=	0
-16	46	-48
-12	24	27
-10	119	-118
-6	68	64
-4	48	48
-2	128	-131
0	182	-176
2	169	176
4	19	-12
8	42	40
10	67	-63
H=	6, K=	1
-14	42	41
-13	51	52
-11	43	-38
-10	36	37
-9	33	-30
-8	65	-61
-6	43	-44
-5	47	45
-4	135	-129
-3	38	-36
-2	28	-26
-1	93	91
0	69	65
1	238	-242
2	86	-89
3	187	188
4	129	-140
5	88	89
6	22	-24
8	37	39
9	22	23
11	57	-54
H=	6, K=	2
-11	42	44
-9	95	-89
-8	65	64
-7	40	37
-6	83	-87
-3	83	-84
-2	23	23
-1	301	301
0	149	152
1	115	-112
2	58	56
3	79	83
4	16	14
5	20	-15
6	32	32
7	20	18
8	91	95
10	23	-20
H=	6, K=	3
-12	27	-24
-11	53	-53
-10	104	108
-9	72	74
-8	125	-118
-7	44	-40
-6	18	17
-5	61	-63
-4	22	21
-3	31	33
-2	87	89
-1	167	165
0	36	33
1	75	-72
2	98	-88
3	42	35
5	20	-24
6	57	59
8	43	46
9	22	24
11	42	41
H=	6, K=	4
-13	19	-27
-11	79	83
-9	98	-98
-8	59	-59
-7	75	80
-4	18	-15
-3	106	-108
-2	35	-36
-1	83	-79
1	219	-228
2	56	-52
4	20	12
5	57	57
6	28	-28
8	44	-44
11	50	48
H=	6, K=	5
-12	22	-22
-10	18	20
-9	26	26
-8	32	-32
-6	38	41
-5	34	-34
-4	21	19
-3	48	-44
-2	44	-41
-1	66	-70
0	31	-35

Table 1 (*cont.*)

1	86	94
3	34	36
4	32	31
6	30	-29
8	43	45
10	63	63
H= 6, K= 6		
-10	43	45
-9	23	-22
-8	19	-20
-6	74	83
-4	31	-30
-3	48	-53
-2	24	20
-1	64	71
0	42	43
1	29	27
2	38	39
6	57	60
7	26	25
8	49	51
9	33	-32
H= 6, K= 7		
-13	31	-30
-12	23	18
-11	37	31
-7	32	32
-6	38	-36
-5	27	-29
-4	92	-96
0	62	-60
1	118	123
3	78	-81
4	27	-29
5	31	-30
8	30	-34
10	40	39
H= 6, K= 8		
-8	35	-34
-7	35	35
-6	40	-41
-5	49	-53
-3	23	-20
-2	16	-15
0	38	-37
1	62	64
2	29	-33
3	51	-53
5	20	24
6	62	-61
7	44	43
9	39	-36
H= 6, K= 9		
-12	25	-24
-10	26	-25
-9	26	-26
-8	23	19
-7	17	-13
-6	64	65
-5	30	30
-3	26	29
-2	43	-43
0	39	-39
2	87	94
3	27	-32
5	29	35
8	44	-46
H= 6, K= 10		
-10	25	23
-7	21	26
-6	42	47
-4	35	32
-3	23	-23
-2	45	44
-1	95	-102
1	32	-32
3	26	-27
6	22	21
8	20	21
H= 6, K= 11		
-10	38	38
-9	20	-14
-8	35	-38
-4	36	34
-1	51	-53
0	59	-62
3	40	-39
5	34	33
6	24	28
7	20	21
H= 6, K= 12		
-8	33	-33
-7	50	-47
-6	20	24
-3	38	37
-2	76	-74
-1	78	82
4	23	-17
H= 6, K= 13		
-8	28	-30
-5	27	25
-4	54	-53
-3	28	30
-2	34	36
-1	26	-25
1	30	28
3	22	-19
4	52	-49
H= 6, K= 14		
-4	19	19
-3	40	-42
0	46	44
H= 6, K= 15		
-2	24	26
H= 7, K= 0		
-12	27	-29
-10	23	20
-8	39	34
-4	251	-259
-2	108	-102
0	70	70
2	42	35
4	77	-84
6	22	-21
8	82	-84
H= 7, K= 1		
-15	37	41
-13	81	-85
-12	34	-34
-11	83	78
-10	37	32
-8	24	-27
-7	32	33
-6	63	-64
-4	53	52
-3	35	-36
-1	102	101
0	29	33
1	55	55
3	23	-18
6	43	40
7	41	-36
8	59	-56
H= 7, K= 2		
-12	29	30
-8	21	-22
-7	21	20
-6	82	81
-5	21	-18
-4	147	141
-3	82	82
-1	43	-45
0	65	65
1	53	-50
2	21	21
3	48	46
4	31	35
5	66	67
6	19	23
7	14	-22
8	49	-48
9	30	-30
H= 7, K= 3		
-14	20	19
-12	42	-40
-9	47	-47
-8	24	21
-7	54	-56
-5	28	28
-4	78	78
-3	72	73
-2	180	-181
-1	87	-90
0	81	86
1	81	-83
2	63	65
4	43	-44
H= 7, K= 4		
-11	21	-25
-9	22	-26
-8	23	-22
-7	49	52
-6	16	-17
-5	42	-45
-4	35	31
-3	48	50
-2	45	-39
-1	99	-102
0	37	32
1	59	62
2	56	-60
3	24	28
4	86	-86
5	37	36
6	36	38
8	23	-17
9	27	-26
H= 7, K= 5		
-13	20	23
-11	39	-40
-9	40	37
-7	57	57
-6	24	-27
-5	51	-53
-4	63	64
-3	95	96
-2	83	-85
-1	39	-39
0	80	82
1	80	82
3	17	19
4	21	22
7	40	-40
8	60	61
H= 7, K= 6		
-9	33	36
-8	21	22
-7	24	-25
-6	38	-41
-3	49	48
-2	20	-15
6	76	73
7	47	46
H= 7, K= 7		
-13	34	34
-11	31	-30
-8	29	-34
-6	31	-32
-5	23	-25
-3	32	32
-2	29	31
-1	49	-53
4	33	30
5	65	61
6	57	-58
7	30	-31
H= 7, K= 8		
-10	21	-23
-9	22	21
-7	34	-33
-5	31	-30
-4	35	41
-3	26	27
-2	49	49
-1	50	53
0	25	-25
1	21	21
2	21	-19
4	49	-49
6	37	-35
H= 7, K= 9		
-7	26	-26
-6	43	-36
-4	30	33
-3	28	-31
-2	22	22
1	39	-38
2	27	-27
3	17	-10
4	20	20
H= 7, K= 10		
-10	29	29
-8	21	-18
-6	22	23
-4	53	-52
-3	54	-51
-2	24	24
-1	37	38
0	44	-41
2	61	65
3	24	-22
4	46	45
H= 7, K= 11		
-10	34	-30
-9	20	24
-7	19	15
-4	30	25
-2	66	-64
-1	28	33
2	41	39
3	45	44
H= 7, K= 12		
-5	45	45
-4	67	-72
-3	39	-36
H= 7, K= 13		
-2	20	16
0	24	-18
1	28	-25
H= 8, K= 0		
-10	19	-17
-6	129	-130
-4	84	84
-2	51	51
0	90	-91
2	58	-58
6	24	-18
H= 8, K= 1		
-12	19	14
-9	19	16
-7	50	-50
-6	35	36
-4	59	59
-3	34	35
-2	24	26
0	25	29
2	72	72
3	19	-21
4	36	-33
5	32	-31
6	59	-56
7	28	24
H= 8, K= 2		
-13	25	27
-9	27	-26
-8	65	69
-7	28	-32
-6	18	12
-5	51	-52
-4	17	12
-3	32	36
-2	26	-27
-1	16	10
3	31	-33
5	33	-30
6	27	29
H= 8, K= 3		
-11	37	-41
-7	38	38
-6	47	-51
-5	21	22
-4	29	-34
-3	34	-34
1	41	-37
3	49	46
5	93	-90
6	31	-31
7	25	29
H= 8, K= 4		
-9	36	41
-8	36	-32
-7	56	58
-6	43	42
-5	37	-39
-4	44	-45
-3	61	65
-1	21	20
2	23	-24
3	44	-41
4	25	-18
5	30	30
H= 8, K= 5		
-6	57	59
-5	33	-33
-4	64	-65
-3	24	23
0	21	16
1	52	-52
3	89	88
4	55	51
6	22	-23
H= 8, K= 6		
-10	31	30
-9	20	-20
-6	23	21
-5	26	-20
-4	60	-64
-2	39	41
0	74	72
6	24	-21
H= 8, K= 7		
-10	27	23
-9	26	23
-8	57	-62
-7	19	-14
-6	87	89
-4	34	-37
-2	75	77
2	25	-25
3	19	23
4	25	-26
H= 8, K= 8		
-9	36	-33
-6	34	38
-4	20	-23
-3	23	22
-2	29	-25
0	19	-18
1	27	-25
2	19	-23
3	28	26
H= 8, K= 9		
-8	31	-29
-7	27	-24
-6	37	36
-5	65	62
0	29	-27
2	36	30
3	51	-50
H= 8, K= 10		
-7	42	38
-2	19	17
-1	20	18
0	29	26
1	40	-39
H= 8, K= 11		
-6	25	-22
-5	19	-13
H= 9, K= 0		
-10	19	-23
-8	25	27
-2	55	-53
0	31	34
2	19	-14
H= 9, K= 1		
-9	25	-27
-6	29	30
-3	23	-19
-2	42	39
-1	46	-45
1	65	67
3	19	15
H= 9, K= 2		
-9	44	-41
-7	25	22
-6	19	-20
-5	31	34
-1	23	27
0	22	18
1	25	-31
2	52	-52
3	58	-54
4	60	60
H= 9, K= 3		
-8	24	-32
-7	33	32
-6	28	25
-2	32	-30
0	67	-68
1	31	-30
3	19	-16
H= 9, K= 4		
-7	33	-30
-4	37	-35
-3	24	-23
0	26	27
2	30	-27
3	21	22
H= 9, K= 5		
-10	43	39
-9	45	-46
-5	21	-19
1	19	19
H= 9, K= 6		
-9	42	38
-7	40	-38
-4	26	23
-2	22	25
-1	19	-20
H= 9, K= 7		
-7	30	-35
-5	22	25
-2	52	-46
0	36	38
H= 9, K= 8		
-4	39	-35
-2	25	23
-1	35	-35
H= 10, K= 0		
-4	43	-42
-2	90	93
H= 10, K= 1		
-2	28	30
H= 10, K= 3		
-4	47	-45
H= 0, K= 0		
2	492	-463
H= 0, K= 2		
1	583	562
H= 0, K= 3		
3	672	644
H= 1, K= 0		
-4	686	666
-2	691	678
2	682	-682
H= 1, K= 1		
-1	498	-501
0	411	-394
1	549	-559
2	530	-522
H= 1, K= 2		
-4	776	-767
H= 1, K= 3		
-1	650	-619
0	500	477
H= 2, K= 0		
-2	881	-862
H= 2, K= 1		
-2	553	-526
H= 2, K= 2		
-1	689	-689
H= 0, K= 2		
2	916	-870
H= 1, K= 1		
-3	1113	1077
H= 1, K= 2		
-3	1475	1646
H= 1, K= 3		
-2	1171	1173
H= 3, K= 17		
-6	20	13

standard deviations. These were regarded as observed reflections, whereas the remaining reflections were excluded from the refinement procedure and the calculations of Fourier functions. The intensities were corrected for Lorentz and polarization effects (Ottersen, 1973) assuming the monochromator crystal to be half mosaic and half perfect in character.

The atomic scattering factors used were those of Doyle & Turner (1968) for C^0, N^0, O^0, and of Stewart, Davidson & Simpson (1965) for hydrogen.

Crystal data

4-(2′,4′-Dinitrobenzyl)pyridine, γ-DNBP, $C_{12}H_9N_3O_4$, monoclinic, $P2_1/c$, $a=7\cdot214$ (2), $b=13\cdot344$ (5), $c=12\cdot553$ (5) Å, $\beta=102\cdot56$ (3)°. Figures in parentheses are estimated standard deviations in units of the least significant digit given for the corresponding parameter. $V=1179\cdot5$ Å^3; M.W. 259·2; $D_{\text{calc}}=1\cdot460$ g cm^{-3}; $Z=4$; $F(000)=536$.

Structure determination

The phase problem was solved by a computer procedure (Long, 1965) based on a reiterative application of Sayre's equation (Karle, 1964). The 413 values of E, the normalized structure factor, greater than 1·50 were used to generate 16 solutions. The most consistent solution was correct. All carbon, nitrogen, and oxygen atoms appeared in the three-dimensional E function. The fast-Fourier program *ALFF* (Hubbard, Quicksall & Jacobson, 1971) was used to calculate all Fourier syntheses.

The structure model was refined to $R_1=0\cdot156$ $\{R_1=(\sum\lvert F_o-\lvert F_c\rvert\rvert)/\sum F_o$ and $R_2=[\sum w(F_o-\lvert F_c\rvert)^2/\sum wF_o^2]^{1/2}\}$. The introduction of anisotropic thermal parameters for all non-hydrogen atoms followed by least-squares refinement reduced R_1 to 0·082. The program used (*UCLALS*4) was that of Gantzel, Sparks & Trueblood (1960), which minimizes $\sum w(\Delta F)^2$.

Positions for all hydrogen atoms were calculated

Table 2. *Fractional atomic coordinates and thermal parameters with estimated standard deviations* (*all* × 10^5)

See Fig. 1. for the identities of the atoms. The e.s.d. is in the least significant digit given for the corresponding parameter. The temperature factor is $\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	59485 (23)	31299 (12)	40185 (15)	2562 (31)	561 (8)	1093 (14)	570 (26)	514 (32)	478 (17)
O(2)	69375 (27)	45989 (15)	45935 (16)	2788 (38)	809 (11)	1079 (15)	71 (33)	−1292 (38)	148 (21)
O(3)	−18572 (23)	41574 (16)	11279 (19)	1888 (29)	964 (13)	1391 (18)	−90 (31)	−861 (37)	−444 (26)
O(4)	−9097 (29)	31861 (23)	25019 (18)	2864 (43)	1593 (23)	1078 (16)	−2197 (54)	609 (40)	189 (31)
N(1)	79689 (23)	81956 (13)	51564 (13)	2280 (32)	566 (9)	668 (10)	−389 (27)	−188 (28)	−34 (16)
N(2)	58658 (20)	40414 (12)	39770 (13)	1590 (24)	569 (9)	737 (11)	276 (24)	175 (25)	212 (15)
N(3)	−6711 (21)	38725 (15)	19201 (16)	1559 (26)	789 (12)	876 (13)	−238 (28)	460 (29)	−559 (20)
C(1)	70012 (20)	66677 (12)	35922 (13)	1370 (23)	456 (8)	557 (9)	−171 (21)	222 (22)	91 (14)
C(2)	56784 (21)	73642 (13)	37618 (13)	1384 (25)	551 (9)	585 (10)	−65 (24)	36 (24)	10 (16)
C(3)	62214 (25)	81062 (14)	45427 (15)	1929 (31)	535 (10)	668 (11)	47 (28)	325 (30)	−52 (17)
C(4)	92350 (26)	75209 (16)	49837 (17)	1672 (31)	620 (11)	759 (13)	−353 (30)	−455 (32)	138 (20)
C(5)	88332 (23)	67607 (15)	42267 (17)	1326 (26)	531 (10)	828 (14)	17 (27)	−29 (29)	115 (19)
C(6)	65823 (26)	58651 (16)	27238 (17)	1781 (33)	589 (11)	666 (13)	−333 (31)	608 (31)	−172 (19)
C(7)	46727 (22)	53552 (12)	25805 (13)	1683 (27)	428 (8)	537 (9)	−23 (22)	211 (24)	−97 (13)
C(8)	43354 (20)	44953 (12)	31449 (12)	1498 (25)	442 (9)	528 (10)	222 (22)	198 (23)	−52 (14)
C(9)	26180 (23)	39955 (14)	29471 (15)	1661 (28)	450 (8)	610 (11)	32 (26)	496 (28)	−47 (16)
C(10)	11677 (21)	43976 (13)	21671 (14)	1433 (25)	534 (9)	665 (11)	−21 (24)	238 (25)	−339 (16)
C(11)	13760 (29)	52521 (15)	15897 (17)	1941 (34)	532 (10)	704 (13)	218 (30)	−485 (34)	−87 (19)
C(12)	31330 (30)	57206 (15)	18020 (17)	2307 (39)	465 (10)	655 (12)	−79 (31)	−263 (35)	115 (18)

(Seff, 1971) assuming the C–H distance to be 0·95 Å (Churchill, 1973). These were included in the least-squares refinement with isotropic thermal parameters.

Full-matrix least-squares refinement of all positional parameters, anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms converged to give the final error indices, $R_1=0{\cdot}056$ and $R_2=0{\cdot}062$. The 'goodness-of-fit', $\{\sum w(F_o-|F_c|)^2/(m-s)\}^{1/2}$, is 2·02. The number of parameters, s, is 208; m is the number of observations (2300). In the final cycle of least-squares, all shifts were less than 1 % of their standard deviations, except for some involving hydrogen atoms, which were 3 % of their e.s.d.'s. Two regions of negative electron density associated with the nitro nitrogen atoms had previously been reported in the final difference-Fourier synthesis of α-DNBP (Seff & Trueblood, 1968). No similar regions of negative electron density appeared in the final difference map for γ-DNBP. The largest peak in the map was 0·3 e Å^{-3}, about three times the e.s.d. of the electron density, 0·1 e Å^{-3}.

The overdetermination ratio is 11·0. Table 1 is a tabulation of the observed and calculated structure factors (× 10), and the final parameters of the non-hydrogen atoms are listed in Table 2. The final parameters for hydrogen atoms are given in Table 3. Standard deviations were calculated from the correlation matrix ignoring standard deviations in cell parameters.

Table 3. *Fractional atomic coordinates* (× 10^4) *and isotropic thermal parameters with estimated standard deviations for hydrogen atoms*

See Fig. 1 for the identities of the atoms. The e.s.d. is in the units of the least significant digit given for the corresponding parameter.

	x	y	z	B
H(1)	4397 (39)	7329 (21)	3350 (22)	4·3 (5)
H(2)	5360 (46)	8596 (24)	4646 (26)	5·3 (6)
H(3)	10503 (47)	7569 (23)	5423 (25)	5·2 (6)
H(4)	9761 (49)	6293 (25)	4181 (26)	5·5 (6)
H(5)	7572 (43)	5348 (23)	2882 (24)	4·9 (6)
H(6)	6583 (44)	6178 (24)	2060 (28)	5·1 (6)
H(7)	2463 (36)	3475 (22)	3272 (22)	4·1 (5)
H(8)	386 (52)	5520 (27)	1086 (30)	6·0 (7)
H(9)	3258 (39)	6315 (23)	1420 (23)	4·6 (5)

Discussion

Bond lengths and angles are given in Fig. 1, where the numbering of the atoms is indicated. A stereo view of the structure is shown in Fig. 2.

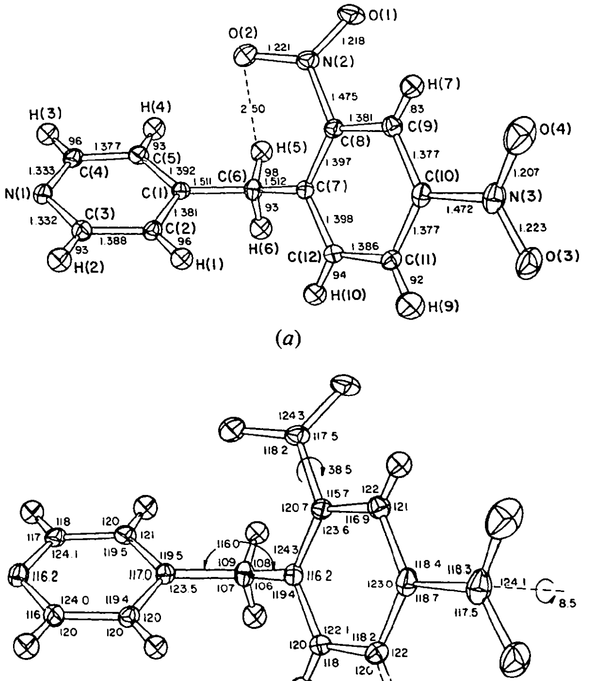
The molecular geometry is in good agreement with the geometry found for α-DNBP (Seff & Trueblood, 1968). The benzyl ring C–C distances average 1·386 Å with an r.m.s. deviation of 0·009 Å, and the pyridine ring has C–C distances of 1·385 Å with an r.m.s. deviation of 0·006 Å. The corresponding values found for α-DNBP are 1·387 (9) and 1·383 (10) Å. The pyridine C–N bond lengths (average 1·333 Å) are somewhat short, but are in good agreement with the corresponding uncorrected C(1)–N(1) distance of 1·331 Å found in α-DNBP.

The C–N bonds at the nitro groups average 1·474 Å with an r.m.s. deviation of 0·001 Å, and the N–O bonds are 1·215 Å with an r.m.s. deviation of 0·007 Å, in agreement with the corresponding uncorrected values of 1·472 and 1·216 Å reported for α-DNBP.

The least-squares planes of each ring and each C–NO$_2$ group are described in Table 4. No atom used to define a plane deviates significantly from that plane. The intramolecular angle between the planes of the two aromatic rings is 70·7°, and the dihedral angle C(2)–C(1)–C(6)–C(7) is 41·3°. (Selected dihedral angles are listed in Table 5.) The plane of the *o*-nitro group is twisted 38·5° from the plane of the benzyl ring, and the plane of the *p*-nitro group is rotated 8·5° in the same sense.

The opening of the benzyl ring angles at C(8), C(10) and C(12) was also found in α-DNBP, and corresponding openings of bond angles have also been reported for *m*-dinitrobenzene (Trotter, 1961).

Based on the molecular structure of α-DNBP, Seff & Trueblood (1968) suggested a two-step reaction mechanism for the tautomerization. The first step was an intramolecular transfer of one of the methylene hy-



(*a*)

(*b*)

Fig. 1. The 4-(2′,4′-dinitrophenyl)pyridine molecule. Ellipsoids of 15 % probability are used (Johnson, 1965). Bond lengths are given in (*a*), and bond angles in (*b*). The e.s.d.'s are 0·002 to 0·003 Å for bonds not involving hydrogen; 0·027 to 0·037 Å for C–H; 0·14 to 0·21° for angles not involving hydrogen; 1·7 to 2·3° for angles involving one hydrogen; and 2·7° for H–C–H.

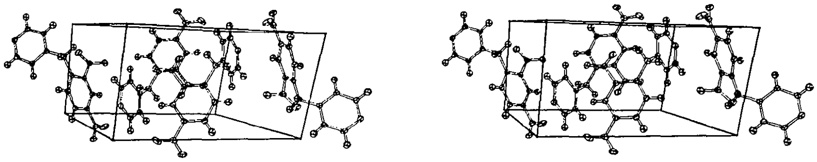


Fig. 2. A stereo view (Johnson, 1965) illustrating the packing of the molecules in the crystal. The view is approximately along the *c* axis; the *b* axis is horizonal and the *a* axis is vertical in the plane of the page. Ellipsoids of 15% probability are used.

Table 4. *Deviations from least-squares planes* (Å × 10^3)

Bold-face deviations indicate the atoms used to define that plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table 2 (Table 3 for hydrogen atoms) lies between that plane and the origin. The direction cosines (× 10^4), q, are with respect to orthogonal axes. The r.m.s. deviation (Å × 10^3) of the bold-face atoms from the plane is δ. D is the distance (in Å) from the plane to the origin.

	Plane 1		Plane 2	Plane 3	Plane 4
N(1)	**2**	C(6)	−99		
C(1)	**2**	C(7)	**−7**	−762	
C(2)	**0**	C(8)	**9**	**2**	
C(3)	**−2**	C(9)	**−7**	763	−202
C(4)	**0**	C(10)	**−2**		**−1**
C(5)	**−2**	C(11)	**7**		162
C(6)	−69	C(12)	**0**		
H(1)	10	N(2)	−10	**−8**	
H(2)	−40	O(1)	−678	**3**	
H(3)	10	O(2)	666	**4**	
H(4)	54	N(3)	−46		**−1**
		O(3)	−225		**−2**
		O(4)	86		**3**
		H(7)	−29		
		H(8)	33		
		H(9)	32		

	Plane 1	Plane 2	Plane 3	Plane 4
$q_{\mathbf{b}\times(\mathbf{a}\times\mathbf{b})}$	−4077	−4452	−7665	−4994
$q_{\mathbf{b}}$	−5941	5609	−127	6400
$q_{\mathbf{a}\times\mathbf{b}}$	6917	6980	6421	5840
D	−3·921 Å	5·035 Å	0·657 Å	5·181 Å
δ	2	6	5	2

Table 5. *Selected dihedral angles* (°)

The e.s.d. given in parentheses is in the least significant digit of the corresponding parameter.

C(2)–C(1)—C(6)–C(7)	41·3 (2)
C(8)–C(7)—C(6)–C(1)	89·9 (2)
C(7)–C(8)—N(2)–O(1)	141·1 (2)
C(7)–C(8)—N(2)–O(2)	40·6 (2)
C(9)–C(10)–N(3)–O(3)	170·2 (2)
C(9)–C(10)–N(3)–O(4)	9·2 (2)

drogen atoms to an oxygen of the *o*-nitro group (O···H, 2·4 Å), shifting the absorption maximum to longer wavelengths. This hydrogen atom might then be transferred intramolecularly to the pyridine nitrogen (O···N, 3·3 Å). A short methylene hydrogen to *o*-nitro oxygen contact [O(2)···H(5), 2·5 Å] is also found in the present structure, and a hydrogen transfer from methylene to the *o*-nitro group may occur. However, γ-DNBP does not have any short contacts (less than 4·0 Å) between O(2) and either an intra- or an intermolecular N(1). Accordingly the second step of the proposed mechanism for the solid-state tautomerization of α-DNBP cannot occur readily in crystalline γ-DNBP. This is the reason, it is proposed, why the γ-DNBP tautomer has a very short solid-state half-life.

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