Structure of the 1:1 Complex of 1-(*p*-Dimethylaminophenyl)-3-(phenylacetyl)urea and 1-Isobutyl-3-(*p*-nitrobenzoyl)urea, C₁₇H₁₉N₃O₂.C₁₂H₁₅N₃O₄

By Akira Uchida, Yuji Ohashi* and Yoshio Sasada

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan

and Masaru Moriya and Tadashi Endo

Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo 157, Japan

Abstract. $M_r = 562 \cdot 63$, triclinic, $P\bar{1}$, $a = 11 \cdot 413$ (3), $b = 16 \cdot 740$ (3), $c = 8 \cdot 569$ (2) Å, $\alpha = 91 \cdot 76$ (3), $\beta = 108 \cdot 24$ (3), $\gamma = 108 \cdot 47$ (2)°, $V = 1459 \cdot 3$ (7) Å³, $D_m = 1 \cdot 28$, $D_x = 1 \cdot 281$ g cm⁻³, $Z = 2$, $T = 293$ K, $F(000) = 298$, $\mu(\text{Mo } K\alpha) = 0 \cdot 99$ cm⁻¹, $\lambda = 0 \cdot 71069$ Å, $R = 0 \cdot 107$ for 3541 observed reflections. The component molecules, linked by the two N–H⋯O hydrogen bonds, make columns along the c axis. The stacking mode of the component containing the dimethylamino group is similar to those found in the crystals of this component itself and of the related mercapto derivative.

Introduction. In order to elucidate the mechanism of the selectivity in oxidation of a pair of thiols, $\text{HSCH}_2(\text{CONH})_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ and $\text{HSCH}_2\text{CH}_2(\text{NHCO})_2\text{—}R$ ($R = \text{alkyl}$), we have determined the crystal structures of the former compound (Uchida, Ohashi, Sasada, Kaneko & Endo, 1983) and its model compound $\text{C}_6\text{H}_5\text{CH}_2(\text{CONH})_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ (Ohashi, Uchida, Sasada, Kinoshita & Endo, 1984). Further studies on the complex formation were carried out using several pairs of acylurea derivatives, $R_1\text{—}(\text{CONH})_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ and $R_2\text{—}(\text{NHCO})_2\text{C}_6\text{H}_4\text{NO}_2$, where R_1 and R_2 are non-polar groups (Endo, Miyazawa, Endo, Uchida, Ohashi & Sasada, 1982; Endo, Miyazawa, Endo, Kato, Uchida, Ohashi & Sasada, 1983). The *p*-nitrophenyl group was used since it has similar shape but opposite electronic character to the *p*-dimethylaminophenyl group and the selectivity for $\text{C}_6\text{H}_4\text{NO}_2$ in the oxidation is approximately the same as that for $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$. The crystal structures of these complexes were expected to reflect the interaction between $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ and R_1 or R_2, which may be correlated to the selectivity in the oxidation. The present work was undertaken using the 1:1 molecular complex containing $\text{CH}_2\text{C}_6\text{H}_5$ as R_1 and $\text{CH}_2\text{CH}(\text{CH}_3)_2$ as R_2.

Experimental. Reddish-purple crystals obtained from an acetonitrile solution, density measured by flotation in cyclohexane/CCl₄; approximate dimensions of crystal $0 \cdot 2 \times 0 \cdot 2 \times 0 \cdot 3$ mm, Rigaku AFC-4 diffractometer, graphite monochromator; cell parameters refined by least-squares method on the basis of 20 independent 2θ values, Mo $K\alpha$ radiation ($19° < 2\theta < 26°$); intensity measurement performed up to $2\theta = 50°$ ($\pm h \pm k + l$ set), θ–2θ scan technique, scan speed 2° min⁻¹ (θ); 5131 reflections measured, 3541 intensities with $|F_o| > 3\sigma(|F_o|)$ considered as observed and used for the structure determination; corrections for Lorentz and polarization, absorption ignored; direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); block-diagonal least squares (*HBLS*, Ohashi, 1975) with anisotropic thermal parameters for all non-H atoms, H atoms located on difference map, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = [\sigma^2(|F_o|) + (C|F_o|)^2]^{-1}$, $C(=0 \cdot 015)$ adjusted so that constant values of $\langle w(|F_o| - |F_c|)^2 \rangle$ were obtained in the different $|F_o|$ and $\sin\theta$ intervals; final $R = 0 \cdot 107$, $R_w = 0 \cdot 072$ for 3541 observed reflections; $(\Delta/\sigma)_{\text{max}} = 0 \cdot 6$; difference-map excursions $<0 \cdot 4$ e Å⁻³; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); no correction for secondary extinction; calculations carried out on the FACOM–HITAC system M-180 computer at this Institute.

Discussion. The final atomic parameters for the non-H atoms are in Table 1.†

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† Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms and bond lengths involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38850 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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* To whom correspondence should be addressed.

Table 1. *Final atomic coordinates* $(\times 10^4)$ *for non-hydrogen atoms and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{1}{3} \sum_i \sum_j B_{ij} a_i^* \, a_j^* \, \mathbf{a}_i . \mathbf{a}_j .$$

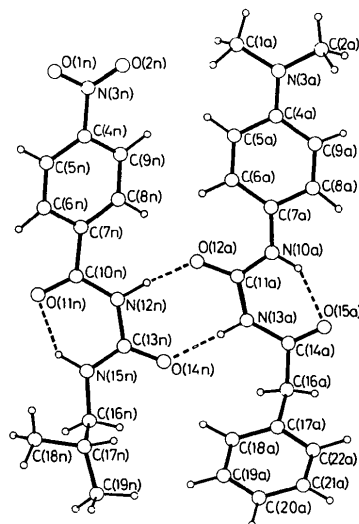|	x	y	z	B_{eq} (Å^2)
O(1n)	2460 (3)	−2751 (2)	3288 (4)	10·3
O(2n)	4360 (3)	−2540 (2)	5080 (4)	9·1
N(3n)	3607 (3)	−2317 (2)	3967 (4)	6·9
C(4n)	4128 (3)	−1497 (2)	3436 (4)	5·1
C(5n)	5401 (3)	−981 (2)	4228 (4)	5·2
C(6n)	5867 (3)	−217 (2)	3721 (4)	5·1
C(7n)	5039 (3)	52 (2)	2429 (4)	4·7
C(8n)	3758 (3)	−492 (2)	1634 (4)	5·1
C(9n)	3298 (3)	−1262 (2)	2113 (4)	5·6
C(10n)	5605 (3)	897 (2)	1988 (4)	5·4
O(11n)	6783 (2)	1217 (2)	2219 (3)	7·1
N(12n)	4722 (3)	1298 (2)	1308 (4)	5·4
C(13n)	4979 (3)	2123 (2)	848 (4)	5·9
O(14n)	4072 (2)	2406 (2)	469 (3)	6·8
N(15n)	6184 (3)	2535 (2)	853 (4)	6·6
C(16n)	6586 (4)	3417 (3)	578 (5)	8·3
C(17n)	7035 (4)	4023 (3)	2205 (6)	9·5
C(18n)	8301 (4)	3958 (3)	3378 (6)	10·6
C(19n)	7163 (7)	4879 (4)	1938 (8)	15·4
C(1a)	−604 (4)	−2839 (2)	5152 (5)	7·4
C(2a)	−2794 (4)	−2744 (3)	4327 (6)	8·4
N(3a)	−1490 (3)	−2411 (2)	4329 (4)	7·0
C(4a)	−1021 (3)	−1648 (2)	3768 (4)	4·9
C(5a)	247 (3)	−1339 (2)	3699 (4)	5·5
C(6a)	702 (3)	−593 (2)	3100 (4)	5·0
C(7a)	−90 (3)	−114 (2)	2548 (4)	4·2
C(8a)	−1346 (3)	−408 (2)	2601 (4)	5·0
C(9a)	−1801 (3)	−1155 (2)	3179 (4)	5·5
N(10a)	294 (2)	658 (2)	1912 (3)	4·7
C(11a)	1403 (3)	1028 (2)	1617 (4)	4·8
O(12a)	2317 (2)	742 (1)	1906 (3)	6·3
N(13a)	1540 (2)	1776 (2)	912 (3)	4·9
C(14a)	657 (3)	2192 (2)	416 (4)	4·8
O(15a)	−400 (2)	1958 (1)	651 (3)	5·9
C(16a)	1112 (3)	2967 (2)	−373 (4)	5·8
C(17a)	1776 (3)	3763 (2)	896 (4)	5·4
C(18a)	3106 (4)	4018 (2)	1729 (5)	7·3
C(19a)	3728 (5)	4771 (3)	2862 (6)	9·0
C(20a)	3034 (5)	5242 (3)	3146 (5)	9·2
C(21a)	1728 (4)	4989 (3)	2336 (5)	8·9
C(22a)	1078 (4)	4250 (2)	1216 (5)	6·9

Fig. 1. Structure of the 1:1 hydrogen-bonded complex of amino-benzyl and nitro-isobutyl molecules with the numbering of the atoms.

The structure of the 1:1 hydrogen-bonded complex is shown in Fig. 1. The two molecules (abbreviated as amino-benzyl and nitro-isobutyl) are linked by two N—H···O hydrogen bonds, as found in the crystals of the SH derivative (1) (Uchida, Ohashi, Sasada, Kaneko & Endo, 1984) and of the amino-benzyl molecule (2) (Ohashi, Uchida, Sasada, Kinoshita & Endo, 1984). The inter- and intramolecular hydrogen-bond lengths are: N(12n)···O(12a) 2·820 (4), O(14n)···N(13a) 2·895 (4), O(11n)···N(15n) 2·705 (4) and N(10a)···O(15a) 2·690 (4) Å.

The conformation of the amino-benzyl molecule is approximately the same as that in (2). The acylurea moiety is planar within ±0·03 Å and its mean plane makes angles of 6·1 (1) and 66·3 (1)° with the benzene rings of the p-dimethylaminophenyl and benzyl groups, respectively. On the other hand, the nitrophenylacyl-urea moiety of the nitro-isobutyl molecule does not take a planar conformation. The torsion angles C(8n)—C(7n)—C(10n)—N(12n), C(7n)—C(10n)—N(12n)—C(13n), C(10n)—N(12n)—C(13n)—N(15n) and N(12n)—C(13n)—N(15n)—C(16n) are 28·4 (5), 176·3 (3), −9·8 (6) and −173·1 (3)°, respectively.

Bond lengths and angles are given in Table 2. The values in the amino-benzyl molecule are in good agreement with the corresponding ones in (1) and (2). The geometry of the acylurea moiety in the nitro-isobutyl molecule is in accordance with that of the amino-benzyl one.

The crystal structure shows that the component molecules, respectively, form columns along the c axis and are packed in sheets parallel to the (2$\bar{1}$0) plane. The projection of one sheet along the a axis is shown in Fig. 2, in which several short intermolecular distances are given. The stacking mode of the amino-benzyl molecules is similar to those found in (1) and (2). Fig. 3(a) shows the projection of the two molecules around the inversion center (0,0,0), along the normal to the mean plane of the acylurea moiety. The stacking mode is approximately the same as that observed in (1) except for the replacement of the SH group by the phenyl group. The distance between the mean planes of the acylurea moieties is 3·546 (3) Å in the present complex and 3·392 (3) Å for (1). Fig. 3 (b) shows the projection of the two molecules around the inversion center (0,0,$\frac{1}{2}$), along the normal to the mean plane of the benzene ring of one p-dimethylaminophenyl group. The stacking mode is similar to that of (2). The dimethylamino group of one molecule is capped by the benzyl group of the other roughly at right angles. The distances between the mean planes are 3·696 (6) Å for the present complex and 3·640 (8) Å for (2). On the other hand, the stacking between the nitro-isobutyl molecules is not so favorable because the nitrophenyl ring is not coplanar with the mean plane of the acylurea moiety.

The color of the crystal may arise from the charge-transfer interaction between the amino-benzyl

molecules, since the present complex is almost colorless in an acetonitrile solution and the stacking of the nitro-isobutyl molecules is unfavorable. The crystal of the SH derivative, which has approximately the same stacking as shown in Fig. 3(a), is pale yellow, whereas the present crystal is reddish purple. The acylurea moiety of the amino-benzyl molecule is hydrogen bonded with the nitro-isobutyl molecule and the electron of the acylurea moiety may be withdrawn by the nitrophenyl group through the N—H···O hydrogen bonds. This brings about the stronger charge-transfer interaction between the p-dimethylaminophenyl group and the acylurea moiety than that of the SH crystal (1).

Although the isobutyl group does not make any short contacts with the p-dimethylaminophenyl group, the benzyl group contacts with the p-dimethylaminophenyl group as shown in (2). This indicates that the interaction between the p-dimethylaminophenyl and benzyl groups, as well as the charge-transfer interaction described above, may play a principal role for the stabilization of the stacking and the interaction would be closely correlated to the shape-specific weak interaction described previously (Endo, Okubo, Kaneko, Uehara, Tasai, Sato, Nikki, Nakagawa & Kamei, 1982).
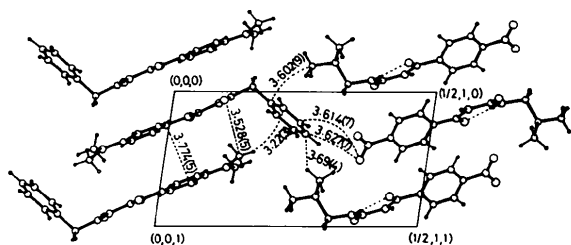

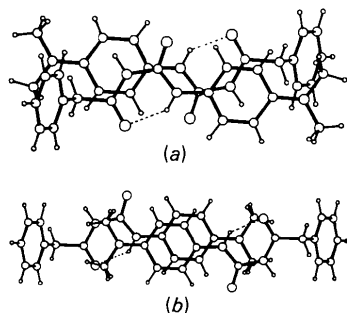Fig. 2. Projection of one sheet on the (2̄10) plane along the a axis. (Distances in Å.)

(a)

(b)

Fig. 3. Overlapping mode of the two amino-benzyl molecules around the inversion centers: (a) (0,0,0) and (b) (0,0,½).

Table 2. *Bond lengths* (Å) *and bond angles* (°)

O(1n)—N(3n)	1·214 (5)	O(1n)—N(3n)—O(2n)	122·8 (4)
O(2n)—N(3n)	1·225 (5)	O(1n)—N(3n)—C(4n)	119·3 (3)
N(3n)—C(4n)	1·461 (5)	O(2n)—N(3n)—C(4n)	118·0 (3)
C(4n)—C(5n)	1·367 (5)	C(3n)—C(4n)—C(5n)	120·4 (3)
C(4n)—C(9n)	1·389 (5)	C(3n)—C(4n)—C(9n)	118·3 (3)
C(5n)—C(6n)	1·361 (5)	C(5n)—C(4n)—C(9n)	121·3 (3)
C(6n)—C(7n)	1·402 (5)	C(4n)—C(5n)—C(6n)	119·6 (3)
C(7n)—C(8n)	1·388 (5)	C(5n)—C(6n)—C(7n)	120·4 (3)
C(7n)—C(10n)	1·472 (5)	C(6n)—C(7n)—C(8n)	118·6 (3)
C(8n)—C(9n)	1·358 (5)	C(6n)—C(7n)—C(10n)	117·1 (3)
C(10n)—O(11n)	1·226 (5)	C(8n)—C(7n)—C(10n)	124·3 (3)
C(10n)—N(12n)	1·376 (5)	C(7n)—C(8n)—C(9n)	121·1 (3)
N(12n)—C(13n)	1·413 (5)	C(4n)—C(9n)—C(8n)	118·9 (3)
C(13n)—O(14n)	1·230 (5)	C(7n)—C(10n)—O(11n)	122·0 (3)
C(13n)—N(15n)	1·328 (5)	C(7n)—C(10n)—N(12n)	115·3 (3)
N(15n)—C(16n)	1·451 (6)	O(11n)—C(10n)—N(12n)	122·7 (3)
C(16n)—C(17n)	1·540 (7)	C(10n)—N(12n)—C(13n)	128·2 (3)
C(17n)—C(18n)	1·519 (8)	N(12n)—C(13n)—O(14n)	117·8 (3)
C(17n)—C(19n)	1·427 (10)	N(12n)—C(13n)—N(15n)	117·5 (3)
C(1a)—N(3a)	1·441 (6)	O(14n)—C(13n)—N(15n)	124·7 (4)
C(2a)—N(3a)	1·414 (6)	C(13n)—N(15n)—C(16n)	121·6 (3)
N(3a)—C(4a)	1·384 (5)	N(15n)—C(16n)—C(17n)	111·0 (4)
C(4a)—C(5a)	1·395 (5)	C(16n)—C(17n)—C(18n)	109·1 (4)
C(4a)—C(9a)	1·392 (5)	C(16n)—C(17n)—C(19n)	112·7 (5)
C(5a)—C(6a)	1·373 (5)	C(18n)—C(17n)—C(19n)	112·1 (5)
C(6a)—C(7a)	1·378 (5)	C(1a)—N(3a)—C(2a)	117·0 (4)
C(7a)—C(8a)	1·376 (5)	C(1a)—N(3a)—C(4a)	120·2 (3)
C(7a)—N(10a)	1·412 (4)	C(2a)—N(3a)—C(4a)	122·2 (4)
C(8a)—C(9a)	1·367 (5)	N(3a)—C(4a)—C(5a)	122·2 (3)
N(10a)—C(11a)	1·328 (4)	N(3a)—C(4a)—C(9a)	122·0 (3)
C(11a)—O(12a)	1·240 (4)	C(5a)—C(4a)—C(9a)	115·7 (3)
C(11a)—N(13a)	1·392 (4)	C(4a)—C(5a)—C(6a)	122·2 (3)
N(13a)—C(14a)	1·370 (5)	C(5a)—C(6a)—C(7a)	120·6 (3)
C(14a)—O(15a)	1·227 (4)	C(6a)—C(7a)—C(8a)	118·2 (3)
C(14a)—C(16a)	1·502 (5)	C(6a)—C(7a)—N(10a)	124·4 (3)
C(16a)—C(17a)	1·511 (6)	C(8a)—C(7a)—N(10a)	117·4 (3)
C(17a)—C(18a)	1·374 (6)	C(7a)—C(8a)—C(9a)	121·1 (3)
C(17a)—C(22a)	1·382 (6)	C(4a)—C(9a)—C(8a)	122·1 (3)
C(18a)—C(19a)	1·401 (7)	C(7a)—N(10a)—C(11a)	128·3 (3)
C(19a)—C(20a)	1·345 (8)	N(10a)—C(11a)—O(12a)	124·1 (3)
C(20a)—C(21a)	1·348 (8)	N(10a)—C(11a)—N(13a)	118·0 (3)
C(21a)—C(22a)	1·379 (7)	O(12a)—C(11a)—N(13a)	117·9 (3)
		C(11a)—N(13a)—C(14a)	128·9 (3)
		N(13a)—C(14a)—O(15a)	122·0 (3)
		N(13a)—C(14a)—C(16a)	114·6 (3)
		O(15a)—C(14a)—C(16a)	123·4 (3)
		C(14a)—C(16a)—C(17a)	111·3 (3)
		C(16a)—C(17a)—C(18a)	119·5 (4)
		C(16a)—C(17a)—C(22a)	121·4 (4)
		C(18a)—C(17a)—C(22a)	119·1 (4)
		C(17a)—C(18a)—C(19a)	119·5 (4)
		C(18a)—C(19a)—C(20a)	120·6 (5)
		C(19a)—C(20a)—C(21a)	119·9 (5)
		C(20a)—C(21a)—C(22a)	121·2 (5)
		C(17a)—C(22a)—C(21a)	119·7 (4)

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