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The Crystal and Molecular Structures of *p*-Nitrobenzylidene-*p*-dimethylaminoaniline and *p*-Dimethylaminobenzylidene-*p*-nitroaniline

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The crystal data for *p*-nitrobenzylidene-*p*-dimethylaminoaniline (I) are: monoclinic, space group $P2_1/c$; $a=11{\cdot}065$ (2), $b=7{\cdot}759$ (2), $c=16{\cdot}488$ (2) Å, $\beta=106{\cdot}53$ (3)°, $Z=4$. The crystal data for *p*-dimethylaminobenzylidene-*p*-nitroaniline (II) are: triclinic, space group $P\bar{1}$; $a=9{\cdot}509$ (1), $b=16{\cdot}200$ (1), $c=9{\cdot}505$ (1) Å, $\alpha=91{\cdot}69$ (1), $\beta=107{\cdot}52$ (1), $\gamma=101{\cdot}04$ (1)°, $Z=4$ (two independent molecules in the asymmetric unit). The intensity data were collected on a four-circle diffractometer using Zr-filtered Mo $K\alpha$ radiation. The structures were refined by a block-diagonal least-squares method to R indices of 0·081 for (I) and 0·070 for (II). The molecule (I), as a whole, is in a nearly planar conformation, and (II) in a non-planar one. The twist angles of the aniline ring out of the C–N=C–C plane are 9·2° for (I), and 41·5 and 49·0° for (II). The twist angles of the benzylidene ring range from 4·1 to 11·4°.

Introduction

The crystal structure analyses of benzylideneaniline (III), benzylideneaniline-*p*-carboxylic acid (IV), *p*-methylbenzylidene-*p*-nitroaniline (V) (Bürgi & Dunitz, 1970) and *N*-(2,4-dichlorobenzylidene)aniline (VI) (Bernstein, 1972) have revealed that the aniline ring in these compounds is considerably twisted out of the plane C–N=C–C. It was pointed out that the resonance interaction between the N lone-pair electrons in the bridge portion and the benzene ring on the aniline side stabilizes the molecule in a twisted conformation. Our interest lies in how the intramolecular charge transfer effect operates on the molecular shape of *p*- and *p'*-substituted benzylideneaniline with a strong electron donor and acceptor. The molecular structure of *p*-nitrobenzylidene-*p*-dimethylaminoaniline (I) determined by ultraviolet and e.s.r. spectra and X-ray diffraction has been published in preliminary form (Ezumi, Nakai, Sakata, Nishikida, Shiro & Kubota, 1974). In the course of our investigation of *p*-dimethylaminobenzylidene-*p*-nitroaniline (II), the results of the ultraviolet spectral study of *p*-substituted benzylideneanilines having nitro and/or dimethylamino groups were reported by Skrabal, Steiger & Zollinger (1975). They concluded that the molecule of (I) is planar or nearly planar and (II) is twisted to a rather reduced extent. The results of the structure determinations for (I) and one of the polymorphs of (II) are here discussed.

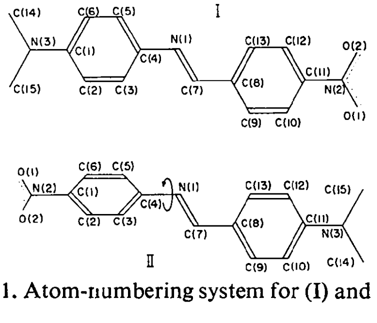

Fig. 1. Atom-numbering system for (I) and (II).

Experimental

Crystals of (I) were recrystallized by slow evaporation from an acetonitrile solution, and crystals of (II) from an acetone solution. Preliminary X-ray photographs gave the space group and the approximate unit-cell dimensions. More accurate cell constants were obtained from a least-squares fit of 12 reflexions on a diffractometer. From the statistical distribution of E values, the centrosymmetric space group $P\bar{1}$ for (II) was assumed and verified after the crystal structure refinement. Crystal data are given in Table 1.

Table 1. *Crystal data of* (I) *and* (II)

	(I)	(II)
$C_{15}H_{15}N_3O_2$		
F.W. 269·3		
Colour	Dark brown	Orange
a	11·065 (2) Å	9·509 (1) Å
b	7·759 (2)	16·200 (1)
c	16·488 (2)	9·505 (1)
α	90·0°	91·69 (1)°
β	106·53 (3)	107·52 (1)
γ	90·0	101·04 (1)
U	1357·0 Å^3	1364·5 Å^3
D_x	1·32 g cm^{-3}	1·31 g cm^{-3}
D_m	1·31	1·30
Z	4	4
Crystal size	0·2 × 0·3 × 0·3 mm	0·3 × 0·3 × 0·3 mm
Linear absorption coefficient (Mo $K\alpha$)	1·08 cm^{-1}	1·07 cm^{-1}
Systematic absent reflexions	$h0l$ when l is odd $0k0$ when k is odd	
Space group	$P2_1/c$	$P\bar{1}$ (or $P1$)
Number of reflexions measured	2475 ($\theta_{max}=27{\cdot}5°$)	3527 ($\theta_{max}=23{\cdot}5°$)

Three-dimensional intensity data were collected on a Hilger and Watts Y-290 diffractometer. Integrated intensities were measured by the θ–2θ scan technique with Mo $K\alpha$ radiation and a scintillation counter. A pulse-height analyser and zirconium filter were used. Each reflexion was integrated in 80 steps at an interval of 0·01°. The measurement time was 1 s per step. Backgrounds were counted for 20 s on both sides of each reflexion. One standard reflexion was measured every 10 reflexions to check any change in crystal setting and any crystal deterioration. No significant change was observed during data collection. All the intensities were corrected for Lorentz and polarization factors, but not for absorption effects [the size of the crystals used was 0·2 × 0·3 × 0·3 mm for (I) and 0·3 × 0·3 × 0·3 mm for (II)].

Structure determination and refinement

(I) *p-Nitrobenzylidene-p-dimethylaminoaniline*

The structure was solved by the method of Beurskens (1963) with a program written by the authors (H. N. & M. S.) on a FACOM 270–30 computer. An E map based on the signs of 243 reflexions ($E \geq 1 \cdot 1$) revealed the positions of all the non-hydrogen atoms. After block-diagonal least-squares refinement, a difference electron density map was calculated, from which the positions of 15 hydrogen atoms were obtained. These coordinates were fixed with isotropic temperature factors of 2·90 Å^2 (deduced from the conventional Wilson plot). Successive anisotropic refinement on the non-hydrogen atoms gave an R value, where $R=\sum||F_o|-|F_c||/\sum|F_o|$, of 0·081 for 1675 reflexions.[*] The reflexions with $|F_c|$ less than twice their standard deviations were rejected at the final refinement. The standard deviation of each reflexion was estimated as described later.

(II) *p-Dimethylaminobenzylidene-p-nitroaniline*

The two crystallographically independent molecules in the asymmetric unit are referred to as molecule A and molecule B. The phase problem was solved by using the program *MULTAN* (Main, Germain & Woolfson, 1970) with local modifications on a FACOM 270–30 computer. Eight solutions with high figures-of-merit were obtained, one of which was a trivial solution of all positive signs. 284 reflexions ($E \geq 1 \cdot 8$) were used for each E map. Two assemblies of the peaks, $\frac{1}{2}$ apart in the direction of the c axis, were found in the asymmetric unit of every E map. The peaks in respective assemblies could be combined in several ways to give a plausible molecular structure. The orientation of the long molecular axis was the same in all the images of the molecule. Trial models of the crystal structure were made up of the combinations of two images chosen from different assemblies, and were selected on the basis of packing considerations. The models of higher peaks were successively examined by the least-squares method. After several trials, one directly led to the correct structure. It was finally confirmed that the signs of 195 E's were correct. The crystal structure thus obtained was refined as for (I), using isotropic temperature factors of 2·66 Å^2 for hydrogen atoms. The R value was 0·070 for 2854 reflexions.[*]

The standard deviation of each reflexion was taken as $\sigma(F_o)=[\sigma_1^2(F_o)+c^2|F_o|^2]^{1/2}$ where $\sigma_1(F_o)$ is the estimated standard deviation depending on the counting errors (Grant, Killean & Lawrence, 1969). The value of c^2 at the final stage of least-squares refinement was 0·00300 for (I) and 0·00295 for (II). The weighting scheme used was $\sqrt{w}=1/\sigma(F_o)$ for $|F_c| \geq 2\sigma(F_o)$ and $\sqrt{w}=0$ for $|F_c|<2\sigma(F_o)$. The refinement was carried out to minimize the function $\sum[w(|F_o|-|F_c|)^2]$. The

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[*] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31569 (30 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

[*] See previous footnote.

Table 2. *Atomic parameters* (× 10^4) *with their estimated standard deviations for* (I)

The anisotropic temperature factor is of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	4953 (3)	4311 (5)	3072 (2)	132 (3)	518 (11)	73 (2)	47 (10)	−27 (4)	−129 (7)
O(2)	3690 (4)	2422 (5)	3352 (2)	257 (5)	411 (9)	50 (1)	108 (12)	8 (4)	25 (6)
N(1)	21 (3)	2862 (4)	−847 (2)	101 (3)	199 (6)	36 (1)	26 (7)	20 (3)	0 (4)
N(2)	4010 (3)	3414 (5)	2870 (2)	139 (4)	298 (8)	53 (2)	133 (9)	8 (4)	−65 (6)
N(3)	−3040 (3)	3185 (4)	−4215 (2)	111 (3)	216 (6)	37 (1)	−30 (7)	16 (3)	−11 (5)
C(1)	−2280 (3)	3137 (4)	−3386 (2)	96 (3)	154 (6)	34 (1)	31 (8)	20 (3)	−13 (5)
C(2)	−1178 (3)	4124 (5)	−3136 (2)	102 (4)	210 (8)	38 (1)	−23 (9)	33 (4)	9 (6)
C(3)	−410 (3)	4051 (5)	−2315 (2)	97 (3)	219 (8)	41 (2)	−38 (9)	33 (4)	−7 (6)
C(4)	−694 (3)	3025 (4)	−1705 (2)	89 (3)	166 (7)	38 (1)	32 (8)	27 (3)	−3 (5)
C(5)	−1795 (3)	2055 (4)	−1957 (2)	117 (4)	178 (7)	38 (1)	−16 (9)	40 (4)	9 (5)
C(6)	−2581 (3)	2110 (5)	−2775 (2)	102 (4)	188 (7)	44 (2)	−59 (8)	37 (4)	−16 (6)
C(7)	941 (3)	3838 (5)	−529 (2)	109 (4)	200 (7)	41 (2)	10 (9)	31 (4)	9 (6)
C(8)	1708 (3)	3702 (4)	350 (2)	92 (3)	187 (7)	35 (1)	31 (8)	25 (4)	−17 (5)
C(9)	2743 (4)	4762 (5)	638 (2)	124 (4)	240 (9)	47 (2)	−48 (10)	29 (4)	−1 (6)
C(10)	3495 (3)	4676 (5)	1453 (2)	92 (4)	261 (9)	59 (2)	−28 (10)	18 (4)	−32 (7)
C(11)	3189 (3)	3533 (5)	1992 (2)	99 (4)	231 (8)	38 (2)	96 (9)	0 (4)	−45 (6)
C(12)	2157 (4)	2492 (6)	1733 (2)	153 (5)	246 (8)	38 (2)	2 (11)	30 (5)	17 (6)
C(13)	1425 (3)	2556 (5)	911 (2)	112 (4)	225 (8)	42 (2)	−32 (10)	15 (4)	−3 (6)
C(14)	−4308 (4)	2470 (6)	−4402 (2)	109 (4)	304 (10)	46 (2)	−23 (11)	7 (4)	−37 (7)
C(15)	−2788 (4)	4440 (6)	−4795 (2)	143 (5)	279 (10)	40 (2)	−2 (11)	21 (4)	18 (7)

Table 2 (*cont.*)

	$x\ (\times 10^3)$	$y\ (\times 10^3)$	$z\ (\times 10^3)$	B
H(C2)	−91	492	−358	2·83
H(C3)	30	470	−217	2·83
H(C5)	−199	127	−151	2·83
H(C6)	−330	142	−292	2·83
H(C7)	119	472	−87	2·83
H(C9)	287	560	24	2·83
H(C10)	412	547	159	2·83
H(C12)	204	179	213	2·83
H(C13)	69	192	74	2·83
H(C14)	−477	268	−497	2·83
H′(C14)	−481	313	−407	2·83
H″(C14)	−426	123	−425	2·83
H(C15)	−188	422	−487	2·83
H′(C15)	−287	564	−459	2·83
H″(C15)	−341	427	−530	2·83

value $\{\sum[w(|F_o|-|F_c|)^2]/(m-n)\}^{1/2}$, where m is the number of structure factors in the summation and n is the number of variables, was 1·208 for (I) and 1·354 for (II). The parameter shifts in the final cycle were smaller than half the corresponding standard deviations. The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The positions of the hydrogen atoms do not deviate far from the positions chemically expected.

Results and discussion

Fig. 1 shows the atom-numbering system of each molecule. The atoms of molecule *B* in the crystal (II) are indicated by the corresponding primed atom number in molecule *A*. For (I) positional and thermal parameters, with their estimated standard deviations, are listed in Table 2. The bond distances and angles involving only heavy atoms are shown in Tables 4 and 5. The corresponding information for (II) is given in Tables 3, 6 and 7. The standard deviation of the difference between corresponding bond lengths in molecule *A* and molecule *B* for (II) is 0·0082 Å. The mean and the largest values of such differences are 0·007 and 0·017 Å respectively, which are not significant, and the weighted averages are given in Table 6. No librational corrections for bond lengths were applied.

Table 3. *Atomic parameters* (× 10⁴) *with their estimated standard deviations for* (II)

Anisotropic temperature factor: $\exp\,[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	8278 (3)	1108 (2)	9852 (3)	335 (6)	50 (1)	263 (5)	115 (4)	183 (9)	71 (4)
O(2)	7413 (3)	1292 (2)	7554 (3)	312 (6)	52 (1)	220 (4)	74 (4)	102 (8)	−30 (4)
N(1)	8134 (3)	4952 (1)	10456 (3)	144 (4)	39 (1)	129 (3)	47 (3)	72 (6)	10 (3)
N(2)	7849 (3)	1549 (2)	8858 (3)	173 (5)	41 (1)	207 (5)	53 (4)	148 (8)	35 (4)
N(3)	7251 (3)	8759 (1)	11271 (3)	150 (4)	35 (1)	162 (4)	40 (3)	88 (7)	10 (3)
C(1)	7899 (3)	2436 (2)	9275 (3)	120 (5)	34 (1)	150 (5)	35 (4)	119 (8)	27 (4)
C(2)	7378 (3)	2936 (2)	8157 (3)	137 (5)	40 (1)	132 (4)	38 (4)	112 (8)	7 (4)
C(3)	7441 (3)	3773 (2)	8533 (3)	138 (5)	43 (1)	113 (4)	53 (4)	83 (8)	25 (4)
C(4)	8023 (3)	4104 (2)	10020 (3)	125 (5)	37 (1)	130 (4)	39 (4)	97 (7)	16 (4)
C(5)	8568 (3)	3587 (2)	11115 (3)	135 (5)	47 (1)	127 (4)	70 (4)	63 (8)	32 (4)
C(6)	8499 (3)	2749 (2)	10746 (3)	148 (5)	44 (1)	142 (5)	68 (4)	111 (8)	43 (4)
C(7)	7048 (3)	5314 (2)	9852 (3)	130 (5)	38 (1)	113 (4)	28 (4)	99 (7)	20 (4)
C(8)	7113 (3)	6205 (2)	10204 (3)	106 (4)	37 (1)	102 (4)	33 (4)	78 (7)	15 (3)
C(9)	5829 (3)	6543 (2)	9709 (3)	108 (4)	42 (1)	113 (4)	22 (4)	64 (7)	22 (4)
C(10)	5848 (3)	7383 (2)	10048 (3)	111 (5)	39 (1)	114 (4)	43 (4)	68 (7)	27 (4)
C(11)	7201 (3)	7925 (2)	10906 (3)	132 (5)	35 (1)	111 (4)	40 (4)	110 (7)	20 (3)
C(12)	8505 (3)	7585 (2)	11384 (3)	117 (5)	40 (1)	129 (4)	21 (4)	68 (7)	13 (4)
C(13)	8455 (3)	6746 (2)	11044 (3)	117 (5)	39 (1)	124 (4)	37 (4)	79 (7)	17 (4)
C(14)	5933 (4)	9124 (2)	10766 (4)	181 (6)	41 (2)	241 (7)	81 (5)	101 (10)	15 (5)
C(15)	8685 (4)	9321 (2)	12040 (4)	202 (6)	37 (2)	251 (7)	34 (5)	114 (11)	−40 (5)
O(1′)	981 (3)	8756 (2)	5742 (3)	237 (5)	59 (1)	378 (6)	121 (4)	122 (9)	−20 (5)
O(2′)	3353 (3)	8989 (2)	6887 (3)	261 (5)	49 (1)	294 (5)	35 (4)	52 (8)	−61 (4)
N(1′)	2214 (3)	5175 (1)	4541 (2)	133 (4)	36 (1)	125 (3)	37 (3)	84 (6)	11 (3)
N(2′)	2167 (3)	8527 (2)	6164 (3)	207 (5)	44 (1)	176 (4)	49 (4)	111 (8)	5 (4)
N(3′)	2842 (3)	1323 (1)	3759 (3)	197 (5)	34 (1)	159 (4)	46 (4)	126 (7)	17 (3)
C(1′)	2202 (3)	7643 (2)	5771 (3)	165 (5)	34 (1)	113 (4)	40 (4)	115 (8)	11 (4)
C(2′)	3554 (3)	7392 (2)	6203 (3)	124 (5)	40 (1)	112 (4)	24 (4)	55 (7)	7 (4)
C(3′)	3579 (3)	6562 (2)	5822 (3)	117 (5)	42 (1)	122 (4)	28 (4)	79 (7)	10 (4)
C(4′)	2245 (3)	6005 (2)	5025 (3)	132 (5)	35 (1)	104 (4)	31 (4)	95 (7)	22 (3)
C(5′)	885 (3)	6284 (2)	4584 (3)	113 (5)	38 (1)	138 (4)	41 (4)	73 (7)	32 (4)
C(6′)	855 (3)	7107 (2)	4981 (3)	120 (5)	44 (1)	142 (5)	47 (4)	100 (8)	32 (4)
C(7′)	2865 (3)	4694 (2)	5446 (3)	112 (4)	40 (1)	117 (4)	31 (4)	77 (7)	18 (4)
C(8′)	2904 (3)	3839 (2)	5000 (3)	105 (4)	34 (1)	109 (4)	26 (4)	90 (7)	15 (3)
C(9′)	3441 (3)	3303 (2)	6051 (3)	142 (5)	43 (1)	96 (4)	47 (4)	72 (7)	21 (4)
C(10′)	3427 (3)	2472 (2)	5666 (3)	158 (5)	42 (1)	109 (4)	50 (4)	74 (8)	30 (4)
C(11′)	2847 (3)	2134 (2)	4176 (3)	122 (5)	36 (1)	131 (4)	31 (4)	109 (7)	15 (4)
C(12′)	2291 (3)	2685 (2)	3099 (3)	115 (5)	40 (1)	107 (4)	27 (4)	64 (7)	13 (4)
C(13′)	2326 (3)	3507 (2)	3508 (3)	107 (4)	38 (1)	103 (4)	31 (4)	55 (7)	17 (4)
C(14′)	3421 (5)	762 (2)	4861 (4)	384 (10)	42 (2)	222 (7)	117 (7)	212 (13)	49 (5)
C(15′)	2095 (4)	961 (2)	2246 (4)	292 (8)	36 (2)	186 (6)	21 (6)	130 (11)	−17 (5)

Table 3 (*cont.*)

	B	$x(\times 10)^3$	$y(\times 10)^3$	$z(\times 10)^3$
H(C2)	691	265	699	2·66
H(C3)	705	417	765	2·66
H(C5)	906	389	1227	2·66
H(C6)	890	233	1150	2·66
H(C7)	596	491	897	2·66
H(C9)	480	616	913	2·66
H(C10)	481	760	961	2·66
H(C12)	956	797	1206	2·66
H(C13)	946	646	1144	2·66
H(C14)	616	971	1099	2·66
H′(C14)	555	911	963	2·66
H″(C14)	498	872	1098	2·66
H(C15)	859	980	1222	2·66
H′(C15)	959	932	1143	2·66
H″(C15)	923	911	1309	2·66
H(C2′)	459	782	681	2·66
H(C3′)	468	637	620	2·66
H(C5′)	−14	584	395	2·66
H(C6′)	−19	733	473	2·66
H(C7′)	341	493	667	2·66
H(C9′)	386	353	715	2·66
H(C10′)	384	209	655	2·66
H(C12′)	187	245	194	2·66
H(C13′)	192	392	270	2·66
H(C14′)	329	24	447	2·66
H′(C14′)	268	63	545	2·66
H″(C14′)	461	106	548	2·66
H(C15′)	208	42	225	2·66
H′(C15′)	80	98	186	2·66
H″(C15′)	267	121	167	2·66

Table 4. *Bond lengths* (Å) *for* (I) *with their estimated standard deviations*

C(1)—C(6)	1·400 (5)	C(12)-C(13)	1·368 (5)
C(1)—C(2)	1·399 (5)	C(4)–N(1)	1·416 (4)
C(2)—C(3)	1·380 (4)	N(1)–C(7)	1·258 (4)
C(3)—C(4)	1·386 (5)	C(7)–C(8)	1·460 (4)
C(4)—C(5)	1·391 (5)	N(2)–C(11)	1·476 (4)
C(5)—C(6)	1·382 (4)	N(2)–O(1)	1·219 (5)
C(8)—C(13)	1·381 (5)	N(2)–O(2)	1·228 (5)
C(8)—C(9)	1·380 (5)	N(3)–C(1)	1·386 (4)
C(9)—C(10)	1·367 (5)	N(3)–C(14)	1·458 (5)
C(10)-C(11)	1·366 (6)	N(3)–C(15)	1·446 (5)
C(11)-C(12)	1·364 (5)		

Table 5. *Bond angles* (°) *for* (I) *with their estimated standard deviations*

N(3)—C(1)—C(2)	120·6 (3)	C(9)—C(10)-C(11)	118·6 (3)
N(3)—C(1)—C(6)	121·6 (3)	C(10)-C(11)-C(12)	121·4 (3)
C(6)—C(1)—C(2)	117·8 (3)	N(2)—C(11)-C(10)	118·8 (3)
C(1)—C(2)—C(3)	120·5 (3)	N(2)—C(11)-C(12)	119·8 (3)
C(2)—C(3)—C(4)	122·2 (3)	C(11)-C(12)-C(13)	119·8 (3)
C(3)—C(4)—C(5)	117·0 (3)	C(12)-C(13)-C(8)	120·2 (3)
N(1)—C(4)—C(3)	126·8 (3)	C(4)—N(1)-C(7)	121·3 (3)
N(1)—C(4)—C(5)	116·3 (3)	N(1)—C(7)-C(8)	122·9 (3)
C(4)—C(5)—C(6)	122·0 (3)	C(11)-N(2)-O(1)	118·2 (3)
C(5)—C(6)—C(1)	120·5 (3)	C(11)-N(2)-O(2)	117·6 (3)
C(7)—C(8)—C(9)	119·3 (3)	O(1)—N(2)-O(2)	124·2 (3)
C(7)—C(8)—C(13)	122·2 (3)	C(1)—N(3)-C(14)	118·4 (3)
C(13)-C(8)—C(9)	118·5 (3)	C(1)—N(3)-C(15)	119·5 (3)
C(8)—C(9)—C(10)	121·5 (3)	C(14)-N(3)-C(15)	118·1 (3)

The least-squares planes through the atoms of C(1) - C(6) (abbreviated as plane 1), C(8) - C(13) (plane 3) and the central grouping atoms C(4), N(1), C(7), C(8) (plane 2) were calculated for the three molecules, as shown in Table 8. These displacements are not large in all the molecules.

The twist angles of both benzene rings out of plane 2 are given in Table 9 along with the data in the previous reports (Bürgi & Dunitz, 1970; Bernstein, 1972). It is shown that molecule (I) is almost planar and (II) is largely twisted just like the molecules of (III), (IV), (V) and (VI).

Table 6. *Bond lengths* (Å) *for* (II) *with their estimated standard deviations*

	Molecule *A*	Molecule *B*	Weighted average
C(1)—C(6)	1·380 (6)	1·384 (8)	1·382 (5)
C(1)—C(2)	1·384 (6)	1·371 (6)	1·377 (4)
C(2)—C(3)	1·379 (5)	1·390 (5)	1·384 (3)
C(3)—C(4)	1·401 (6)	1·393 (8)	1·397 (5)
C(4)—C(5)	1·395 (6)	1·400 (6)	1·398 (4)
C(5)—C(6)	1·377 (5)	1·382 (5)	1·379 (3)
C(8)—C(13)	1·398 (8)	1·405 (6)	1·402 (5)
C(8)—C(9)	1·392 (6)	1·387 (6)	1·390 (4)
C(9)—C(10)	1·385 (4)	1·381 (5)	1·383 (3)
C(10)-C(11)	1·409 (8)	1·408 (6)	1·408 (5)
C(11)-C(12)	1·409 (6)	1·426 (6)	1·417 (4)
C(12)-C(13)	1·375 (5)	1·367 (5)	1·371 (3)
C(4)—N(1)	1·398 (4)	1·400 (5)	1·399 (3)
N(1)—C(7)	1·278 (6)	1·279 (6)	1·279 (4)
C(7)—C(8)	1·456 (4)	1·447 (5)	1·452 (3)
N(2)—C(1)	1·468 (5)	1·479 (5)	1·474 (3)
N(2)—O(1)	1·220 (6)	1·211 (5)	1·215 (4)
N(2)—O(2)	1·214 (5)	1·218 (7)	1·216 (4)
N(3)—C(11)	1·374 (4)	1·360 (4)	1·367 (3)
N(3)—C(14)	1·445 (6)	1·458 (7)	1·451 (5)
N(3)—C(15)	1·452 (9)	1·447 (7)	1·449 (6)

Table 7. *Bond angles* (°) *for* (II) *with their estimated standard deviations*

	Molecule *A*	Molecule *B*
N(2)—C(1)—C(2)	118·1 (2)	118·9 (2)
N(2)—C(1)—C(6)	119·4 (2)	118·0 (2)
C(6)—C(1)—C(2)	122·5 (3)	123·1 (3)
C(1)—C(2)—C(3)	118·7 (2)	118·6 (2)
C(2)—C(3)—C(4)	120·1 (3)	119·8 (3)
C(3)—C(4)—C(5)	119·8 (2)	120·2 (2)
N(1)—C(4)—C(3)	122·2 (2)	122·2 (2)
N(1)—C(4)—C(5)	118·0 (2)	117·4 (2)
C(7)—C(8)—C(9)	120·7 (2)	120·6 (2)
C(7)—C(8)—C(13)	121·5 (2)	121·5 (2)
C(13)-C(8)—C(9)	117·8 (2)	117·7 (2)
C(8)—C(9)—C(10)	122·1 (2)	122·0 (2)
C(9)—C(10)-C(11)	119·9 (2)	120·7 (2)
C(10)-C(11)-C(12)	118·0 (2)	117·2 (2)
N(3)—C(11)-C(10)	121·2 (2)	122·0 (2)
N(3)—C(11)-C(12)	120·9 (2)	120·8 (2)
C(11)-C(12)-C(13)	121·1 (2)	121·0 (2)
C(12)-C(13)-C(8)	121·2 (3)	121·4 (2)
C(4)—N(1)—C(7)	119·6 (2)	120·4 (2)
N(1)—C(7)—C(8)	122·6 (2)	122·9 (2)
C(1)—N(2)—O(1)	117·7 (2)	118·9 (2)
C(1)—N(2)—O(2)	119·1 (2)	117·4 (3)
O(1)—N(2)—O(2)	123·2 (3)	123·7 (2)
C(11)-N(3)—C(14)	121·7 (2)	120·7 (2)
C(11)-N(3)—C(15)	119·9 (2)	121·0 (2)
C(14)-N(3)—C(15)	118·0 (2)	117·9 (2)

Table 8. *Equations of the least-squares planes and deviations* (Å) *of the atoms from the planes*

The equation of plane is of the form: $AX+BY+CZ=D$, where X, Y, Z and D are in Å. Atoms in brackets were not included in the calculation of the best plane.

	(I)		(II) Molecule *A*	Molecule *B*
Plane 1: C(1)–C(6)				
A	−0·6056		0·9618	−0·3896
B	0·7564		0·0646	−0·2655
C	0·4092		−0·4105	0·9582
D	1·0909		3·8675	1·1549
C(1)	−0·006		−0·007	−0·002
C(2)	0·003		0·005	−0·001
C(3)	0·000		0·003	−0·001
C(4)	−0·001		−0·010	0·007
C(5)	−0·002		0·008	−0·011
C(6)	0·005		0·001	0·008
[N(1)	0·003		0·011	−0·065]
[N(3)	−0·028	N(2)	0·017	−0·012]
[C(14)	0·276	O(1)	−0·025	−0·055]
[C(15)	0·149	O(2)	0·100	0·009]
Plane 2: C(4), N(1), C(7), C(8)				
A	−0·7168		−0·6149	0·9134
B	0·6432		−0·2023	0·1665
C	0·4621		0·8958	−0·5064
D	0·7634		2·5096	1·1419
C(4)	−0·003		−0·015	0·009
N(1)	0·003		0·013	−0·008
C(7)	0·003		0·016	−0·009
C(8)	−0·003		−0·015	0·009
[C(1)	0·030		−0·030	0·054]
[C(11)	−0·011		−0·032	−0·104]
Plane 3: C(8)–C(13)				
A	−0·6700		−0·4557	0·9534
B	0·6958		−0·2158	0·0971
C	0·4388		0·9573	−0·4067
D	0·9885		4·0279	1·3025
C(8)	−0·004		0·006	0·001
C(9)	0·009		−0·006	−0·003
C(10)	−0·005		0·001	0·003
C(11)	−0·005		0·005	−0·001
C(12)	0·011		−0·006	−0·001
C(13)	−0·006		0·000	0·001
[C(7)	0·003		0·025	−0·073]
[N(2)	−0·043	N(3)	0·024	0·029]
[O(1)	−0·112	C(14)	0·009	0·040]
[O(2)	0·008	C(15)	−0·093	−0·120]

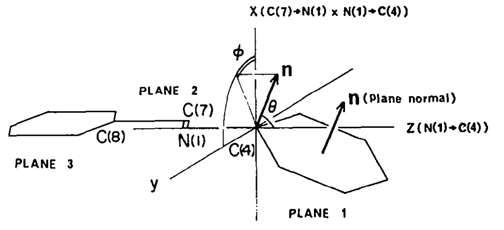

Fig. 2. Definition of the angles φ and θ. **n** represents the normal to plane 1. The axes of the Cartesian coordinate system are shown as x, y and z.

Table 9. *Twist angles of aniline and benzylidene rings out of the plane of the central grouping atoms*

φ and θ are defined as shown in Fig. 2.

	Dihedral angle (between 1 and 2)	φ	θ	Dihedral angle (between 3 and 2)	φ	θ
(I)	9·2°	9·1°	89·8°	4·1°	4·3°	90·2°
(II) Molecule *A*	41·5	41·0	90·8	−11·4	−10·5	90·8
Molecule *B*	49·0	48·5	93·0	−7·7	−6·9	92·9
(III)	55·2	55·0	92·6	−10·3	−10·2	90·9
(IV)	41·1	41·1	88·4	−13·7	−13·3	90·5
(V)	50·2	49·9	96·1	−8·1	−7·9	93·6
(VI)	37·9	36·8	91·4	6·1	6·8	89·5

The mean C–C bond lengths in both benzene rings C(1) – C(6) and C(8) – C(13) are 1·390 and 1·371 Å in (I); and 1·386 and 1·395 Å in (II). The bond distances C(4)–N(1) and C(7)–C(8) are shortened and N(1)=C(7) is lengthened in (I) and (II), in comparison with those in (III) (1·460, 1·496 and 1·237 Å respectively). A similar trend is found in (IV), (V) and (VI). It was concluded that the contributions of the quinoid structure to the resonance forms are significant in these compounds.

The bond angles in both the benzene rings of (I) and (II) are compatible with those in the related compounds mentioned above. The internal angles of the C atom substituted by the electron-withdrawing group tend to be relatively large. In (I), the angle C(3)–C(4)–N(1) is largely deformed to reduce the repulsive interaction between H(3) and H(7). This deformation and the slight twist of the aniline ring result in elongation of the non-bonded distance H(3)–H(7) to 2·09 Å.

The three atoms of the nitro group and the C atom bonded by the nitro group are, within the experimental errors, coplanar in each molecule. The N atom of the dimethylamino group in (I) deviates by 0·16 Å from the plane connecting C(1), C(14), C(15). The corresponding distances in molecule *A* and molecule *B* of (II) are both 0·05 Å approximately. The substituents deviate from the plane of the benzene ring to which they are attached (Table 8).

The crystal structures of (I) and (II) are shown in Figs. 3 and 4. The short intermolecular distances are listed in Tables 10 and 11. The molecules of (I) are arranged in the crystal with their long molecular axes approximately parallel to [101]. The stacking of the two molecules which are inversely related is shown in Fig. 5. The distance between the planes 2 of these two molecules is 4·23 Å. The crystal of (II) may be described as consisting of alternating layers of molecule *A* and molecule *B* stacked in the **c** direction. Molecules *A* and *B* are arranged in respective layers as shown in Fig. 6, which is the projection viewed vertically down on plane 2. The distances between the planes 2 of the adjacent molecules which are related by the inversion centres are 2·96 and 2·88 Å in the layer of molecule *A*, and 4·29 and 4·40 Å in the layer of molecule *B*. It is apparent that different types of packing effect operate on the geometries of molecule *A* and molecule *B*.

Table 10. *Short intermolecular distances* (Å) *for* (I)

The roman numerals as superscripts refer to the equivalent position relative to the reference molecule at x,y,z:

(i) $-x, \quad -y, \quad -z$
(ii) $-x, \quad 1-y, \quad -z$
(iii) $1-x, \quad -\tfrac{1}{2}+y, \quad \tfrac{1}{2}-z$
(iv) $-x, \quad -\tfrac{1}{2}+y, \quad -\tfrac{1}{2}-z$
(v) $-x, \quad \tfrac{1}{2}+y, \quad -\tfrac{1}{2}-z$
(vi) $1+x, \quad \tfrac{1}{2}-y, \quad \tfrac{1}{2}+z$

C(5)–C(12^{i})	3·582	C(7)—C(8^{ii})	3·579
O(1)–C(14^{ii})	3·528	O(2)—C(10^{iii})	3·711
N(1)–C(8^{ii})	3·511	N(3)—C(9^{iv})	3·620
N(2)–C(1^{ii})	3·532	C(13)–C(15^{iv})	3·618
C(3)–C(12^{ii})	3·592	C(9)—C(14^{v})	3·684
C(5)–C(10^{ii})	3·399	O(1)—C(6^{vi})	3·575
C(7)–C(7^{ii})	3·562	C(10)–C(14^{vi})	3·552

Table 11. *Short intermolecular distances* (Å) *for* (II)

The roman numerals as superscripts refer to the equivalent position relative to the reference molecule at x,y,z:

(i) $-1+x, \quad y, \quad -1+z$
(ii) $1-x, \quad 1-y, \quad 1-z$
(iii) $-x, \quad 1-y, \quad 1-z$
(iv) $1-x, \quad 1-y, \quad 2-z$
(v) $2-x, \quad 1-y, \quad 2-z$
(vi) $1-x, \quad 2-y, \quad 2-z$

C(2′)—C(10)	3·65	C(5′)—C($7'^{\mathrm{iii}}$)	3·60
C(5′)—C(13^{i})	3·65	C(6′)—C($8'^{\mathrm{iii}}$)	3·61
C(6′)—C(12^{i})	3·67	N(2)—C(14^{iv})	3·68
C(12′)–C(6^{i})	3·65	C(10′)–C(11^{iv})	3·54
C(13′)–C(5^{i})	3·64	N(2)—C(12^{v})	3·56
N(1′)—C(3^{ii})	3·49	C(1)—C(13^{v})	3·57
C(4′)—C(3^{ii})	3·51	O(2′)—C(14^{vi})	3·56
C(2′)—C($11'^{\mathrm{ii}}$)	3·49		

For (III), Bürgi & Dunitz (1971) calculated the potential energy as a function of the twist angle of the aniline ring by adding π-electron and non-bonded interaction energy terms. π-electron energy at a given angle was calculated taking account of the resonance interaction between the N lone-pair electrons in the bridge portion and the π-electrons of the aniline ring. The twist angle at which a potential minimum is observed is consistent with the experimental result on non-planar geometry. The molecules of benzylideneaniline *N*-oxide (Kubota, Yamakawa & Mori, 1963; Koyano & Tanaka, 1965) and *N*-salicylideneaniline (Bregman, Leiserowitz & Schmidt, 1964) in which such resonance interaction is prevented, on the contrary, are planar (Ezumi *et al.*, 1974). In *p*- and *p*′-substituted benzylideneanilines with an electron donor and acceptor, there occurs intramolecular charge transfer between these substituents (*CT*-1). In molecules possessing a strong electron-withdrawing group at the aniline ring, strong intramolecular charge transfer from the bridge N lone-pair electron to this group (*CT*-2) is also possible. The contribution of *CT*-2 to stabilization of the molecule increases with increasing twist angle. On the other hand, the smaller the twist angle, the larger is the contribution of *CT*-1. The molecules of (II), (IV) and (V) thus result in a twisted conformation of the angle between 0° and 90°. It is found that the C(4)–N(1) distance decreases with increasing *CT*-2 effect in the order of (III), (IV), (II) ≈ (V), and that the contribution of the quinoid structure throughout the whole molecule (*CT*-1 effect) is significant, especially in the bridge portion, in the resonance forms considered in (II), (IV) and (V). Since *CT*-2 force is not effective in (I), the molecule in which *CT*-1 is dominant has a planar conformation. Skrabal, Steiger & Zollinger (1975) argued that (I) is almost planar and benzylidene-*p*-dimethylaminoaniline is less planar than (I), both in solution. The twist angles of the benzylidene rings of all the molecules mentioned hitherto range from 4 to 14°, which are of the same order as those of *trans* stilbene (Finder, Newton & Allinger, 1974; Bernstein, 1975).

Planar benzylideneanilines are also found in crystals of the metastable form of *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline (VII) (Bernstein & Schmidt, 1972) and *p*-bromobenzylidene-*p*-bromoaniline (VIII) (Bernstein & Izak, 1975). In the free state, these molecules are more stable in a twisted conformation than in a planar

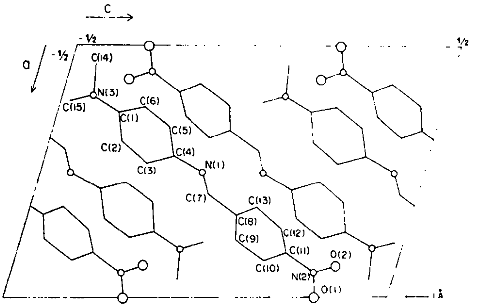

Fig. 3. Crystal structure of (I), viewed down the *b* axis.

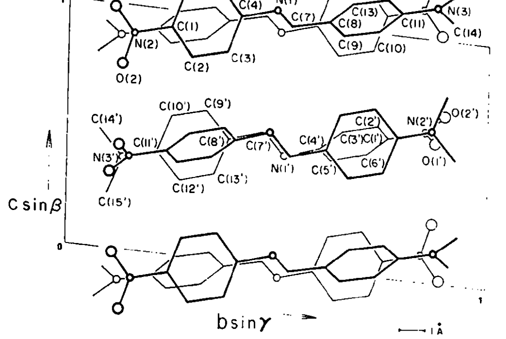

Fig. 4. Crystal structure of (II), viewed down the *a* axis.

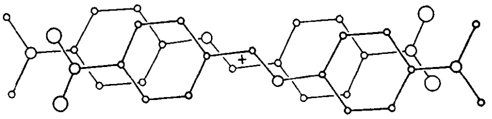

Fig. 5. Overlap between molecules of (I) at x,y,z, and $-x, 1-y, -z$, viewed vertically down on the plane of the central grouping atoms. The cross represents the position of an inversion centre.

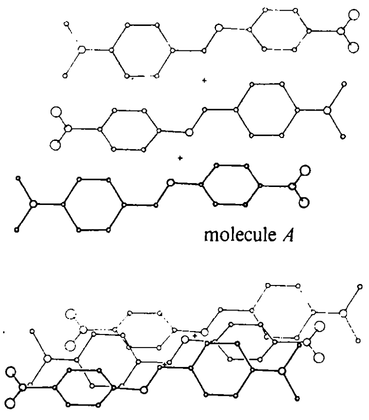

Fig. 6. Molecular stacking in the layer of molecule A and in the layer of molecule B for (II). The molecules are projected vertically on the plane of the central grouping atoms. The cross shows the position of an inversion centre.

one. The difference in the potential energies was estimated by them to be 1·5–2·0 kcal/mol for (VII), and about 3 kcal/mol for (VIII). It was suggested that the loss of the potential energy is compensated by the packing effect in each crystal. The packing effect on the molecular geometry is also found in the crystal of (II) in which the two independent molecules are twisted differently. The molecular shapes in different crystal fields will be determined in further investigations of the polymorphs of (II).

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Stereochemistry of Unsaturated Amino Sugars. I. The Crystal and Molecular Structure of Peracetylated 2,3-Dideoxy-α-D-*threo*-aldopyranose

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1,4,6-Tri-*O*-acetyl-2-(*N*-acetylacetamido)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranose crystallizes in the space group $P2_12_12_1$ with $a=8·332$, $b=13·644$, $c=16·345$ Å, $Z=4$. The structure was solved by direct methods and refined to an R of 0·038. The sugar ring appears in the ${}^0H_5$ half-chair conformation.

Introduction

A new class of unsaturated amino sugars has been synthesized and their infrared and NMR spectra studied (Pravdić & Fletcher, 1969; Pravdić, Židovec & Fletcher, 1970; Pravdić, Židovec & Fletcher, 1973; Pravdić, Židovec, Franjić & Fletcher, 1973).

The following acetylated 2-(*N*-acetylacetamido)-1,2-