

The Structures of Polymorphs of *N*-(*p*-Dimethylaminobenzylidene)-*p*-nitroaniline

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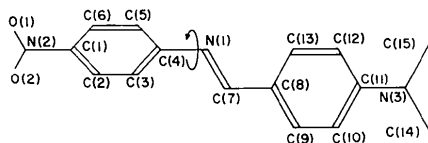
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Abstract

Three polymorphic forms (II), (III) and (IV) of the title compound ($C_{15}H_{15}N_3O_2$) have been investigated [(I) has already been reported]. (II) is triclinic, space group $P\bar{1}$, with $a = 7.507(1)$, $b = 16.704(1)$, $c = 11.051(1)$ Å, $\alpha = 92.79(1)$, $\beta = 90.30(1)$, $\gamma = 96.58(1)^\circ$, $Z = 4$. (III) is monoclinic, space group $P2_1/c$, with $a = 3.989(1)$, $b = 10.621(1)$, $c = 31.932(2)$ Å, $\beta = 95.10(1)^\circ$, $Z = 4$. (IV) is orthorhombic, space group $P2_12_12_1$, with $a = 64.297(13)$, $b = 10.789(1)$, $c = 7.731(1)$ Å, $Z = 16$. $R = 0.063$ (2825 reflexions) for (II), 0.054 (1462) for (III), and 0.081 (3383) for (IV). The twist angles of the aniline group out of the central C–N=C–C plane are almost equal in (I), (II) and (III), and their mean value is 44.8° . In (IV), the four independent molecules adopt various conformations (the twist angles range from 15.1 to 50.4°). The molecular conformations observed in these forms are discussed on the basis of crystal packing.

Introduction

Crystals of *N*-(*p*-dimethylaminobenzylidene)-*p*-nitroaniline are obtained in the four polymorphic forms referred to as (I), (II), (III) and (IV). The geometry of the molecules in solution has been proposed from an ultraviolet spectral study (Skrabal, Steiger & Zollinger, 1975), and that in crystals of (I) from an X-ray study (Nakai, Shiro, Ezumi, Sakata & Kubota, 1976). All of these studies showed the non-planar structure of the molecule. Thus, we carried out the crystal structure analyses of (II), (III) and (IV) in order to see whether this is an inherent nature of the molecule.



Experimental

Crystals of (II) were obtained by slow evaporation from a benzene–acetone solution, and (IV) was obtained from an acetone solution at 273 K. In both solutions, the crystals of (III) were accompanied by those of (II) and (IV), but they were easily identified because of the difference in color. Crystal data not given in the *Abstract* are listed in Table 1. The centrosymmetric space group $P\bar{1}$ was first assumed for (II) from the statistical distribution of the E values and was later confirmed by refinement of the crystal structure.

Three-dimensional intensity data were collected on a Hilger & Watts Y-290 diffractometer. Integrated intensities were measured by the θ - 2θ scan technique with $Cu K\alpha$ radiation. A pulse-height analyzer and a Ni filter were used. The intensity of each reflexion was measured by integrating over 80 steps at 0.01° intervals. The measurement time was 1 s per step. Background was counted for 20 s at each end of the scan. All the intensities were corrected for Lorentz and polarization factors, but not for absorption effects.

Structure determination and refinement

The structures were solved by use of the program *MULTAN* (Main, Germain & Woolfson, 1970) with local modifications on a FACOM 270-30 computer. A

Table 1. *Additional crystal data for (II), (III) and (IV)*

	(II)	(III)	(IV)
U (Å ³)	1374.8	1347.7	5363.1
D_x (Mg m ⁻³)	1.301	1.327	1.334
D_m (Mg m ⁻³)	1.31	1.32	1.32
Crystal size (mm)	$0.4 \times 0.3 \times 0.2$	$0.4 \times 0.1 \times 0.1$	$0.4 \times 0.1 \times 0.1$
Color	Orange	Reddish orange	Red
Linear absorption coefficient μ (Cu $K\alpha$) (mm ⁻¹)	0.848	0.867	0.867
Systematically absent reflexions		$l = 2n + 1$	$h = 2n + 1$
$h0l$			$k = 2n + 1$
$h00$		$k = 2n + 1$	$l = 2n + 1$
$0k0$		$(l = 2n + 1)$	
$00l$			
Number of reflexions measured (θ_{max})	3442 (55.0°)	1835 (57.0°)	3907 (55.0°)

Table 2. Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^2$) with e.s.d.'s in parentheses ($B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$)

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}		<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Form (II), molecule <i>A</i>					Form (IV), molecule <i>A</i>				
O(1)	7865 (3)	8496 (1)	179 (2)	974 (8)	O(1)	362 (1)	6351 (5)	-153 (9)	790 (20)
O(2)	6422 (3)	8420 (1)	1851 (2)	882 (7)	O(2)	324 (1)	8290 (5)	479 (9)	776 (19)
N(1)	7252 (2)	4758 (1)	679 (1)	491 (5)	N(1)	1290 (1)	7657 (5)	1780 (7)	382 (12)
N(2)	7176 (3)	8108 (1)	1011 (2)	646 (5)	N(2)	433 (1)	7310 (5)	350 (9)	566 (20)
N(3)	8039 (3)	1010 (1)	1307 (2)	608 (5)	N(3)	2225 (1)	8992 (5)	4059 (7)	442 (14)
C(1)	7214 (2)	7241 (1)	951 (2)	487 (5)	C(1)	656 (1)	7429 (5)	683 (8)	324 (14)
C(2)	6452 (3)	6793 (1)	1876 (2)	521 (5)	C(2)	727 (1)	8604 (6)	1224 (9)	442 (19)
C(3)	6462 (3)	5969 (1)	1810 (2)	500 (5)	C(3)	939 (1)	8678 (6)	1599 (8)	387 (17)
C(4)	7233 (2)	5591 (1)	813 (2)	455 (5)	C(4)	1076 (1)	7647 (6)	1443 (9)	414 (17)
C(5)	7946 (3)	6063 (1)	-124 (2)	529 (5)	C(5)	988 (1)	6544 (6)	895 (8)	396 (17)
C(6)	7976 (3)	6877 (1)	-54 (2)	522 (5)	C(6)	778 (1)	6426 (6)	511 (7)	377 (17)
C(7)	7727 (2)	4369 (1)	1575 (2)	475 (5)	C(7)	1371 (1)	8551 (6)	2624 (8)	389 (17)
C(8)	7739 (2)	3509 (1)	1529 (1)	449 (5)	C(8)	1581 (1)	8631 (6)	3016 (7)	312 (15)
C(9)	8519 (3)	3125 (1)	2452 (2)	495 (5)	C(9)	1662 (1)	9641 (6)	4069 (9)	463 (20)
C(10)	8636 (3)	2312 (1)	2393 (2)	536 (5)	C(10)	1872 (1)	9666 (6)	4363 (8)	396 (18)
C(11)	7946 (3)	1823 (1)	1385 (2)	501 (5)	C(11)	2020 (1)	8899 (6)	3700 (8)	378 (17)
C(12)	7130 (3)	2209 (1)	457 (2)	513 (5)	C(12)	1940 (1)	7990 (6)	2592 (8)	354 (17)
C(13)	7036 (3)	3022 (1)	523 (2)	476 (5)	C(13)	1736 (1)	7838 (6)	2262 (8)	369 (17)
C(14)	9006 (4)	629 (2)	2200 (3)	840 (7)	C(14)	2291 (1)	10013 (8)	5215 (11)	669 (26)
C(15)	7476 (5)	545 (1)	183 (3)	885 (8)	C(15)	2378 (1)	8108 (7)	3279 (11)	519 (22)
Form (II), molecule <i>B</i>					Form (IV), molecule <i>B</i>				
O(1)	1194 (4)	8587 (1)	2717 (2)	1010 (7)	O(1)	341 (1)	8585 (5)	5672 (8)	708 (18)
O(2)	2551 (4)	8715 (1)	4430 (2)	1062 (8)	O(2)	351 (1)	6769 (5)	4603 (7)	621 (14)
N(1)	2633 (2)	5005 (1)	3283 (1)	526 (5)	N(1)	1284 (1)	7404 (5)	6830 (7)	405 (14)
N(2)	1981 (3)	8314 (1)	3546 (2)	699 (5)	N(2)	438 (1)	7602 (5)	5245 (7)	426 (14)
N(3)	3145 (3)	1240 (1)	4066 (2)	612 (5)	N(3)	2216 (1)	6049 (5)	9141 (7)	474 (17)
C(1)	2128 (3)	7452 (1)	3489 (2)	529 (5)	C(1)	653 (1)	7533 (6)	5780 (8)	398 (19)
C(2)	2884 (3)	7122 (1)	4472 (2)	542 (5)	C(2)	765 (1)	6496 (6)	5309 (9)	422 (17)
C(3)	3024 (3)	6313 (1)	4432 (2)	522 (5)	C(3)	976 (1)	6435 (6)	5665 (7)	368 (15)
C(4)	2414 (2)	5822 (1)	3410 (2)	462 (5)	C(4)	1069 (1)	7428 (5)	6480 (8)	308 (14)
C(5)	1680 (3)	6176 (1)	2428 (2)	523 (5)	C(5)	961 (1)	8499 (5)	6868 (8)	356 (15)
C(6)	1513 (3)	6982 (1)	2477 (2)	518 (5)	C(6)	757 (1)	5868 (6)	6503 (8)	363 (15)
C(7)	2286 (2)	4552 (1)	4173 (2)	485 (5)	C(7)	1361 (1)	6490 (6)	7609 (7)	326 (15)
C(8)	2574 (2)	3711 (1)	4141 (2)	479 (5)	C(8)	1590 (1)	6318 (5)	7917 (8)	342 (15)
C(9)	1969 (3)	3228 (1)	5089 (2)	508 (5)	C(9)	1658 (1)	5416 (5)	8904 (8)	333 (15)
C(10)	2163 (3)	2426 (1)	5077 (2)	537 (5)	C(10)	1867 (1)	5206 (5)	9343 (8)	352 (15)
C(11)	2986 (3)	2040 (1)	4090 (2)	514 (5)	C(11)	2012 (1)	6114 (6)	8699 (9)	389 (17)
C(12)	3629 (3)	2535 (1)	3131 (2)	523 (5)	C(12)	1939 (1)	7104 (6)	7605 (8)	390 (17)
C(13)	3426 (3)	3339 (1)	3173 (2)	517 (5)	C(13)	1726 (1)	7166 (6)	7257 (8)	368 (17)
C(14)	2554 (4)	751 (1)	5087 (3)	810 (8)	C(14)	2304 (1)	5062 (7)	10190 (11)	565 (23)
C(15)	4081 (4)	853 (1)	3100 (2)	770 (8)	C(15)	2366 (1)	6876 (9)	8444 (10)	638 (25)
Form (III)					Form (IV), molecule <i>C</i>				
O(1)	-1454 (7)	1110 (2)	6834 (1)	770 (7)	O(1)	2157 (1)	4738 (6)	4870 (8)	777 (19)
O(2)	583 (7)	2967 (2)	6903 (1)	768 (7)	O(2)	2137 (1)	3095 (6)	6495 (8)	749 (17)
N(1)	2626 (5)	1930 (2)	5002 (1)	413 (5)	N(1)	1206 (1)	3679 (4)	4076 (7)	361 (12)
N(2)	-120 (6)	2031 (2)	6695 (1)	525 (5)	N(2)	2059 (1)	3954 (6)	5538 (8)	561 (17)
N(3)	5073 (6)	3023 (2)	3067 (1)	481 (5)	N(3)	252 (1)	2334 (5)	2483 (8)	445 (17)
C(1)	637 (6)	2007 (2)	6255 (1)	400 (5)	C(1)	1838 (1)	3848 (6)	5216 (8)	404 (17)
C(2)	2273 (6)	3024 (2)	6099 (1)	419 (5)	C(2)	1727 (1)	2912 (6)	5999 (8)	400 (18)
C(3)	2906 (6)	3021 (2)	5680 (1)	407 (5)	C(3)	1511 (1)	2843 (6)	5600 (8)	409 (18)
C(4)	1885 (6)	2000 (2)	5421 (1)	367 (5)	C(4)	1415 (1)	3675 (5)	4538 (7)	280 (14)
C(5)	299 (6)	982 (2)	5594 (1)	406 (5)	C(5)	1532 (1)	4707 (5)	3865 (9)	410 (17)
C(6)	-361 (7)	981 (2)	6006 (1)	413 (5)	C(6)	1750 (1)	4723 (6)	4151 (9)	439 (17)
C(7)	2187 (6)	2903 (2)	4766 (1)	390 (5)	C(7)	1114 (1)	2630 (6)	4064 (8)	391 (18)
C(8)	3055 (7)	2938 (2)	4336 (1)	364 (5)	C(8)	887 (1)	2587 (5)	3665 (7)	284 (15)
C(9)	2145 (7)	3973 (2)	4081 (1)	410 (5)	C(9)	779 (1)	1494 (6)	3942 (9)	445 (18)
C(10)	2788 (6)	4013 (2)	3663 (1)	414 (5)	C(10)	567 (1)	1404 (6)	3642 (9)	482 (20)
C(11)	4402 (6)	3011 (2)	3481 (1)	394 (5)	C(11)	457 (1)	2366 (6)	2867 (9)	429 (18)
C(12)	5328 (7)	1957 (2)	3739 (1)	406 (5)	C(12)	572 (1)	3515 (6)	2667 (8)	426 (18)
C(13)	4697 (6)	1938 (2)	4154 (1)	390 (5)	C(13)	776 (1)	3578 (5)	3003 (8)	369 (15)
C(14)	4229 (8)	4126 (3)	2806 (1)	570 (8)	C(14)	145 (1)	1149 (8)	2681 (12)	681 (26)
C(15)	6404 (9)	1924 (3)	2872 (1)	577 (9)	C(15)	141 (1)	3433 (8)	1839 (10)	612 (23)

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Form (IV), molecule <i>D</i>				
O(1)	2159 (1)	257 (5)	9814 (8)	712 (18)
O(2)	2138 (1)	1841 (6)	11421 (8)	776 (19)
N(1)	1196 (1)	1216 (5)	9247 (6)	375 (14)
N(2)	2058 (1)	1103 (5)	10506 (8)	524 (17)
N(3)	261 (1)	2780 (5)	7506 (8)	501 (17)
C(1)	1835 (1)	1131 (6)	10182 (8)	362 (17)
C(2)	1714 (1)	2069 (6)	10922 (9)	432 (18)
C(3)	1507 (1)	2116 (5)	10680 (8)	336 (15)
C(4)	1414 (1)	1193 (6)	9611 (8)	340 (16)
C(5)	1535 (1)	306 (6)	8975 (8)	381 (17)
C(6)	1738 (1)	199 (5)	9275 (7)	347 (15)
C(7)	1104 (1)	2252 (5)	9000 (8)	337 (15)
C(8)	894 (1)	2415 (5)	8678 (10)	420 (20)
C(9)	806 (1)	3538 (6)	8019 (9)	439 (18)
C(10)	602 (1)	3659 (5)	7665 (7)	342 (14)
C(11)	463 (1)	2639 (6)	7907 (8)	342 (15)
C(12)	541 (1)	1574 (6)	8549 (9)	457 (19)
C(13)	751 (1)	1449 (6)	8924 (8)	388 (17)
C(14)	171 (1)	3964 (8)	6856 (12)	713 (28)
C(15)	122 (1)	1710 (7)	7573 (11)	578 (23)

difference electron density map was calculated after block-diagonal least-squares refinement and revealed the positions of the H atoms. Successive refinement of the positional and anisotropic thermal parameters of the non-hydrogen atoms gave the *R* values ($R = \sum |\Delta F| / \sum |F_o|$) of 0.063 (2825 reflexions) for (II), 0.054 (1462) for (III), and 0.081 (3383) for (IV).

The parameter shifts in the final cycle were smaller than half the corresponding standard deviations. A difference electron density map calculated using the final positional parameters of the non-hydrogen atoms showed no significant peaks other than those due to the H atoms.

The standard deviation of the structure factor was estimated as $\sigma(F_o) = [\sigma_1^2(F_o) + c^2|F_o|^2]^{1/2}$, where $\sigma_1(F_o)$ is the standard deviation due to the counting errors (Grant, Killeen & Lawrence, 1969). The values of c^2 at the final stage of the least-squares refinement were 0.00424 for (II), 0.00138 for (III) and 0.00295 for (IV). The weighting scheme was $w = 1/\sigma^2(F_o)$ for $|F_c| \geq \sigma(F_o)$ and $w = 0$ for $|F_c| < \sigma(F_o)$ or $|\Delta F| \geq 3\sigma(F_o)$. The least-squares refinement was carried out to minimize the function $\sum (w|\Delta F|^2)$. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).*

* Lists of structure factors, thermal parameters of the non-hydrogen atoms, positional parameters of the hydrogen atoms, and bond lengths and angles involving only non-hydrogen atoms for (II), (III) and (IV) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35668 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results and discussion

Final positional and isotropic thermal parameters of the non-hydrogen atoms are given in Table 2. The two independent molecules in (II) are named molecule *A* and molecule *B*, and the four in (IV) molecules *A–D*. The mean estimated standard deviations for *x*, *y* and *z* are 0.002 Å for (II) and (III), and 0.006 Å for (IV).

The molecule in (I) adopts a non-planar conformation, and exhibits a quinoid structure due to the substituent effects. The contribution of the quinoid structure to the bonds C(4)–N(1), C(7)–C(8) and N(1)=C(7) which are in the bridge portion is remarkable: the former two bonds are shortened and the third is lengthened in comparison with those in *N*-benzylideneaniline (Nakai *et al.*, 1976).

The twist angles of the aniline and benzylidene rings out of the central plane in (II) and (III) are very similar to those in (I) (α and β in Table 3). The geometries of the three bonds in the bridge portion are very close to those in (I) (Table 4). In (IV), the four independent molecules take various conformations, three of which are less twisted than those in the other three forms (Table 3). These molecules might be subjected differently to the contribution of the quinoid structure varying with the twist angles. The bond distances observed in the bridge portion, however, were so irregular that the influence of the quinoid structure could not be confirmed.

As the values of α and β (Fig. 1) are respectively 9.2 and 4.1°, *p*-dimethylamino-*N*-(*p*-nitrobenzylidene)aniline can be regarded as a planar molecule (Ezumi, Nakai, Sakata, Nishikida, Shiro & Kubota, 1974; Skrabal, Steiger & Zollinger, 1975; Nakai *et al.*, 1976). Molecule *A* in (IV) may be considered to adopt a planar conformation.

Table 3. Twist angles (°) of the benzene rings of the aniline (α) and benzylidene (β) parts out of the plane of the central-group atoms [C(4), N(1), C(7), C(8)], with *e.s.d.*'s in parentheses

		α	β
α and β are defined in Fig. 1.			
(I)*	molecule <i>A</i>	41.5 (2)	−11.4 (2)
	molecule <i>B</i>	49.0 (2)	−7.7 (2)
(II)	molecule <i>A</i>	45.8 (2)	−9.7 (2)
	molecule <i>B</i>	43.1 (2)	−8.7 (2)
(III)		43.7 (3)	−7.6 (3)
(IV)	molecule <i>A</i>	15.1 (6)	−8.4 (7)
	molecule <i>B</i>	50.4 (6)	−6.9 (6)
	molecule <i>C</i>	28.3 (6)	11.1 (6)
	molecule <i>D</i>	37.1 (6)	−14.6 (6)

* Nakai *et al.* (1976).

Table 4. Comparison of C(4)–N(1), N(1)=C(7) and C(7)–C(8) bond distances (Å)

	C(4)–N(1)	N(1)=C(7)	C(7)–C(8)
(I)* molecule A	1.398 (4)	1.278 (6)	1.456 (4)
molecule B	1.400 (5)	1.279 (6)	1.447 (5)
(II) molecule A	1.394 (3)	1.281 (3)	1.436 (3)
molecule B	1.394 (3)	1.280 (3)	1.444 (3)
(III)	1.398 (5)	1.282 (5)	1.446 (5)
(IV) molecule A	1.400 (9)	1.276 (9)	1.387 (9)
molecule B	1.409 (9)	1.257 (9)	1.503 (9)
molecule C	1.390 (9)	1.277 (9)	1.493 (9)
molecule D	1.430 (9)	1.279 (9)	1.384 (10)
<i>N</i> -Benzylidene-aniline†	1.460 (3)	1.237 (3)	1.496 (3)

* Nakai *et al.* (1976).

† Bürgi & Dunitz (1971).

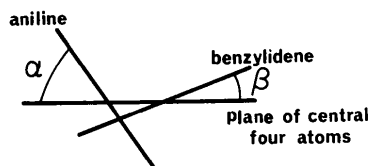


Fig. 1. Schematic representation of the twist angles of the aniline and benzylidene rings as seen from the top to the bottom of the molecule. The molecule is divided into three parts (nitrobenzene ring, C–N=C–C in the bridge portion, and dimethylamino-benzene ring) which are drawn schematically using three lines. When the rings are rotated relatively, as shown here, the α and β values of the molecules listed in Table 3 have opposite sign.

The crystal structures are shown in Fig. 2. The molecules with their long molecular axes nearly vertical to the projection plane lie at almost equal elevation from the plane. If it is supposed that these molecules form a layer structure, the crystal structures may be described as consisting of such layers stacked along the **b**, **b**, **c** and **a** directions in (I), (II), (III) and (IV) respectively. In all forms, one molecule is surrounded by six neighbors in the layer. The dipoles adhered to the two surroundings, which are crystallographically equivalent, are directed almost parallel to that of the central molecule, but those of the other four are antiparallel to the central one. A row of the molecules with their dipoles parallel to each other is straight in (I) and (III) but zigzag in (II) and (IV). The molecules in each row of (III) and (IV) are oriented to form stackings of aniline–aniline and/or benzylidene–benzylidene parts. In (IV), stackings of aniline–benzylidene type are also formed between adjacent rows (Figs. 2 and 3). The distances between the rings are 3.4–3.5 Å. Intermolecular contacts of this kind are not found in (I) and (II). In (III) and (IV), the molecules are packed more densely than in (I) and (II); the values of D_x are 1.310, 1.301, 1.327 and 1.334 Mg m⁻³ for (I), (II),

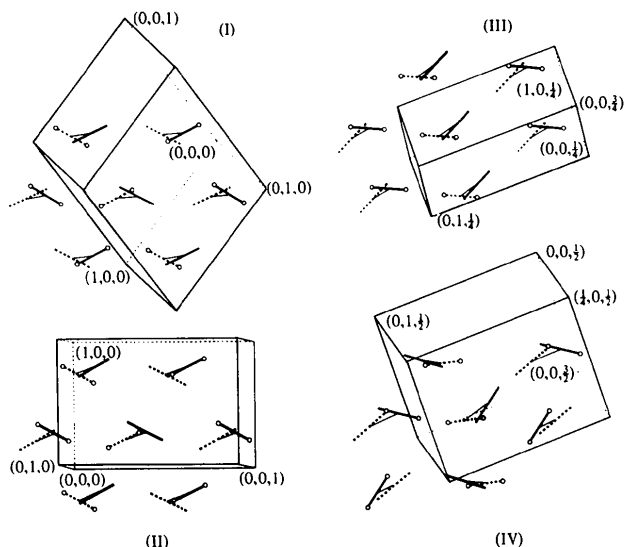


Fig. 2. Crystal structures of (I), (II), (III) and (IV). (III) is bound between $z = \frac{1}{2}$ and $\frac{3}{4}$, and (IV) between $x = 0$ and $\frac{1}{4}$. The molecules are shown schematically as in Fig. 1. The benzene ring at higher elevation is shown by a thick line and that at lower elevation by a dotted line. The nitrobenzene ring is represented by a line with two circles, which indicate the positions of the O atoms.

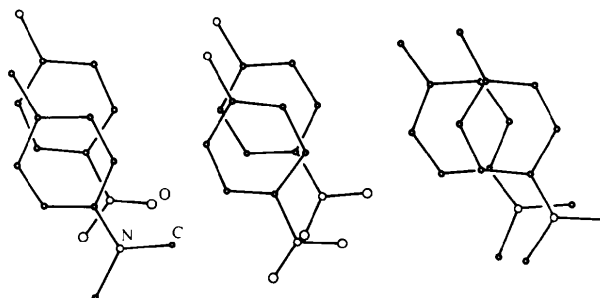


Fig. 3. Stacking of the rings observed in (IV).

(III) and (IV) respectively. The intermolecular contacts between the aniline and benzylidene rings, found only in (IV), are considered to be due to the π – π charge-transfer force.

The values of α are 40–55° in the crystals of *p*-substituted derivatives of *N*-benzylideneaniline which take the non-planar conformation, while the values of β range from 4 to 14°, which are of the same order as those of *trans*-stilbene. Energy calculations and spectral studies on *N*-benzylideneaniline show that the α at the potential minimum agrees well with that observed in the crystal ($\alpha = 55^\circ$), and the conformation exhibited in the crystal is similar to that in solution (Bürgi & Dunitz, 1971). The molecular conformations of (I), (II) and (III) are considered to be closely related to the stable one in the free state. The less twisted molecules in (IV), therefore, are of

high-energy geometry. In (IV), the loss in total conformational energy might be compensated by lowering the lattice energy due to the intermolecular π - π charge-transfer interaction as described above.

Comparison of the powder diffraction patterns at 298 and 403 K revealed that all the forms are transformed to the fifth form (V) at 403 K, and that the diffraction pattern of (V) is very similar to that of (II). The transition temperatures measured by differential thermal analysis are 371–391 K, 341 K, 343–383 K, and 356 K for (I), (II), (III) and (IV) respectively. (V) is transformed into (II) at 298 K, but no definite transition point can be found during the cooling process. In (V) the arrangement of dipoles oriented parallel to each other is probably zigzag as in (II) and (IV), in contrast to the straight arrangement in (I) and (III) (Fig. 2). We suppose that the transitions to (V) on heating (I) and (III) accompany rearrangement of these dipoles and, hence, occur over a wide temperature range.

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The Structure of 2,2',4,4',6,6'-Hexa-*tert*-butylbenzil*

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Abstract

The structure of the title compound and a refinement of the parent compound, benzil, have been carried out. The first is $C_{38}H_{58}O_2$, monoclinic, space group $P2_1/c$, $a = 9.973$ (1), $b = 15.796$ (1), $c = 22.006$ (2) Å, $\beta = 90.140$ (7)° at 115 K giving $Z = 4$ and $D_c = 1.05$ Mg m^{-3} . R_F is 6.4% for 2905 observed reflections. The crystals were bright yellow blocks of square cross section somewhat elongated along [100]. The benzene rings are non-planar because of the crowding of the central part of the molecule. Benzil itself is $C_{14}H_{10}O_2$, hexagonal, $P3_121$, $a = 8.4091$ (8), $c = 13.672$ (2) Å,

at 298 K, $Z = 3$ and $D_c = 1.249$ Mg m^{-3} . R_F is 3.2% for 411 observed reflections up to 125° 2θ with Cu $K\alpha$ radiation.

Introduction

The structure of 2,2',4,4',6,6'-hexa-*tert*-butylbenzil has been determined as part of a continuing study of hindered azobenzene derivatives and related compounds (Le Page, Gabe & Wang, 1981; Le Page, Gabe, Wang, Barclay & Holm, 1980). The structure of benzil itself (Brown & Sadanaga, 1965) has been refined from diffractometer data to allow comparisons to be made on results of similar accuracy.

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