l'intermédiaire de liaisons hydrogène et de contacts de van der Waals (Figs. 4 et 5).

En effet l'espace libre entre les feuillets est occupé par les ions bromure et des molécules de méthanol de cristallisation. Les ions bromures sont à l'origine des liaisons hydrogène (Tableau 6): $O(9^i) \cdots Br(27^{iv})$ avec un angle $O(9^i)-H(90^i) \cdots Br(27^{iv}) = 159°$. Remarquons que l'anion Br^- n'est pas directement lié à l'atome N(16), contrairement à ce qui se passe dans la scopolamine. Ceci est dû, vraisemblablement, à l'encombrement au niveau de l'atome N(16) par le groupement butyle.

D'autres liaisons courtes dûes au méthanol sont aussi à signaler comme: $C(17^i) \cdots O(29^v)$ (liaison du type C—H $\cdots$ O). Enfin des contacts de van der Waals s'établissent entre les feuillets: $O(11^i) \cdots C(23^v)$; $C(8^i) \cdots O(21^{iv})$; $O(9^i) \cdots C(18^{iii})$; $Br(27^i) \cdots C(14^{iii})$.

Conclusions

Les différences de conformation observées entre le bromhydrate de hyosciamine et le bromure de N-butyl-hyosciamine sont sans aucun doute apportées par le groupement butyle qui masque le pôle cationique N^+. Ceci entraîne une conformation différente de la molécule étudiée au niveau du carbone asymétrique.

Or quand on sait le rôle important attribué au pôle cationique dans l'activité biologique de ces molécules, il faut peut être voir là l'explication de la différence de leur comportement en thérapeutique.

Références

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B26, 274–285.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
KUSSÄTHER, E. & HAASE, J. (1972). *Acta Cryst.* B28, 2896–2899.
PAULING, P. & PETCHER, T. I. (1969). *J. Chem. Soc.* p. 1001.

Crystal and Molecular Structure of Some Thermochromic Schiff Bases

By I. Moustakali-Mavridis and E. Hadjoudis

Nuclear Research Center 'Demokritos', Chemistry Department, Aghia Paraskevi Attikis, Athens, Greece

and A. Mavridis

University of Athens, Physical Chemistry Department, 13a Navarinou Str., Athens 144, Greece

The structures of the Schiff bases, N-salicylidene-2-aminopyridine (I), 3-methyl-N-(3-methoxysalicylidene)-2-aminopyridine (II), N-(5-bromosalicylidene)-2-aminopyridine (III) and 5-chloro-N-(5-methoxysalicylidene)-2-aminopyridine (IV) were determined by X-ray crystallographic methods. The molecules are planar and arranged in stacks along the shortest axis with similar interplanar distances. CNDO/2 calculations were carried out on (I) to rationalize the planarity of the system.

Introduction

The crystalline salicylideneanilines are classified as photochromic or thermochromic (Cohen, Schmidt & Flavian, 1964). The photochromic compounds develop an absorption band near 480 nm upon irradiation with UV light, while the thermochromic exhibit an absorption band at room temperature in the same spectral region which diminishes with decreasing temperature.

Both processes are reversible and mutually exclusive. Since the same compound may occur in dimorphs of which one is thermochromic and the other photochromic, it seems that the crystal structure determines the above behaviour, rather than the molecule as such. From the crystal structure determination of the thermochromic N-(5-chlorosalicylidene)aniline (Bregman, Leiserowitz & Schmidt, 1964) and the photochromic 2-chloro-N-salicylideneaniline (Bregman, Leiserowitz &

Osaki, 1964) the hypothesis has been advanced that molecules exhibiting thermochromy are planar, while those exhibiting photochromy are non-planar.

It has been found that a series of N-salicylidene-2-aminopyridine derivatives (Hadjoudis & Xexakis, 1976), belonging to a variety of space groups, show thermochromism. An X-ray structure determination has been carried out on N-salicylidene-2-aminopyridine (I), 3-methyl-N-(3-methoxysalicylidene)-2-aminopyridine (II), N-(5-bromosalicylidene)-2-aminopyridine (III) and 5-chloro-N-(5-methoxysalicylidene)-2-aminopyridine (IV) (Fig. 1), in order to investigate any structural similarities.

Experimental

All the salicylidene-2-aminopyridines were synthesized by well known methods (Vogel, 1966). Single crystals in the form of needles were obtained by cooling solutions in n-heptane. Crystals $0.5 \times 0.25 \times 0.15$ mm mounted along the longest axis were used.

The space groups were determined by photographic and diffractometric methods. The lattice parameters were obtained from diffractometer measurements by a least-squares method from the angular coordinates of 12 reflections in the range $45 < 2\theta < 70°$. The density was measured by flotation in $AgNO_3$ solution. Crystal data are summarized in Table 1.

Diffraction data were collected at room temperature with Cu $K\alpha$ radiation on a Picker four-circle diffractometer controlled by a Digital Equipment Corp. 4K PDP-8 computer (FACS-I system) coupled to a DEC 32K disk file and an Ampex TMZ-7-track tape transport. The intensities were measured by a wandering ω-step scan procedure (Wyckoff et al., 1967) with balanced Ni/Co filters located between the direct Cu $K\alpha$ X-ray beam and the crystal to measure back-
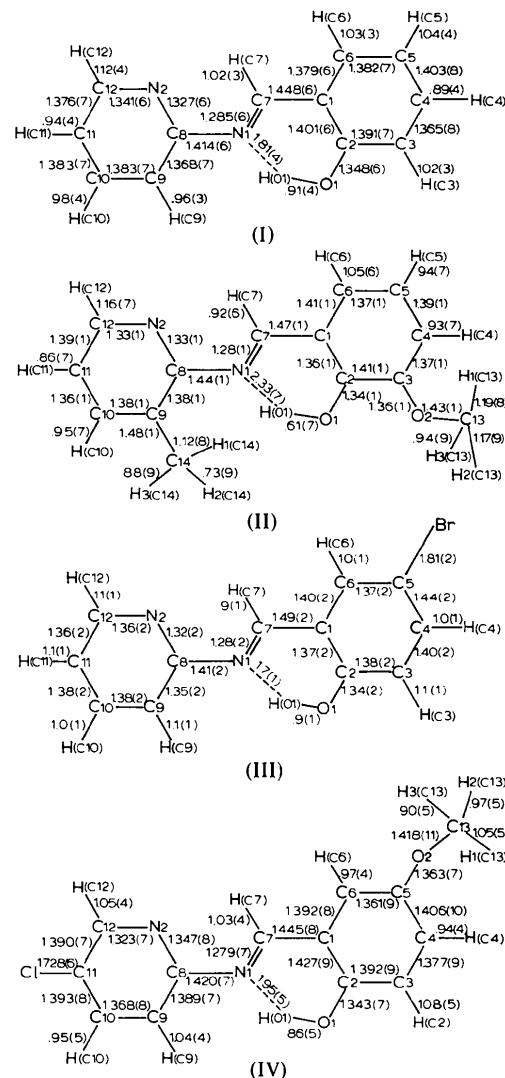

Fig. 1. Bond distances (Å) and atom-numbering system for (I), (II), (III) and (IV). E.s.d.'s in parentheses.

Table 1. Crystal data

	(I)	(II)	(III)	(IV)
	$C_{12}H_{10}N_2O$	$C_{14}H_{14}N_2O_2$	$C_{12}H_9BrN_2O$	$C_{13}H_{11}ClN_2O_2$
FW	198.23	242.28	277.13	262.70
Space group	Pbca	Pbca	P2₁/c	P2₁/c
a (Å)	6.329 (1)	6.656 (1)	8.179 (1)	5.448 (1)
b (Å)	14.778 (3)	14.721 (4)	17.536 (4)	8.139 (1)
c (Å)	21.808 (5)	25.622 (4)	8.978 (2)	27.276 (4)
β (°)	90	90	121.16 (2)	92.70 (2)
U (Å³)	2039.7	2510.5	1101.9	1208.1
D_m^{23} (g cm⁻³)	1.30	1.27	1.71	1.44
D_x^{25} (g cm⁻³)	1.29	1.28	1.67	1.44
Z	8	8	4	4
F(000)	832	1024	552	544
$\mu_{Cu\ K\alpha}$ (cm⁻¹)	6.91	7.18	54.3	27.7
Number of reflections measured	1274	1549	1180	1360
Number of systematically absent reflections	126	257	52	103
Number of reflections used	733	913	926	1024

ground. The alignment and X-ray damage of the crystals were monitored every 100 reflections and automatically corrected for with a new orientation matrix if the crystal was misaligned (Vandlen & Tulinsky, 1971).

The intensities were corrected for absorption (North, Phillips & Mathews, 1968). The observable limit for the accidentally absent reflections was fixed by the average value of the measured intensity of the systematically absent reflections. The intensities were then converted

Table 2. *Summary of the structure determination and refinement*

	(I)	(II)	(III)	(IV)
Minimum value of E used	1·28	1·40	1·30	1·40
Number of signs determined	180	188	205	200
Consistency index	0·69	0·67	0·98	0·84
R based on coordinates of E map	0·173	0·218	0·183	0·214
R at the introduction of anisotropic refinement	0·120	0·136	0·144	0·108
Final R	0·049	0·085	0·079	0·046
Data/parameter ratio (hydrogens not included)	5·4	5·6	6·4	6·3
Maximum residual density (e Å^{-3})	0·10	0·19	0·23	0·17
Minimum residual density	−0·15	−0·26	−0·24	−0·23

Table 3. *Positional parameters and peak heights for* (I) *with e.s.d.'s in parentheses*

	x	y	z	Peak height (e Å^{-3})
C(1)	0·7292 (7)	0·3906 (3)	0·3628 (2)	4·4
C(2)	0·7485 (7)	0·3510 (3)	0·4209 (2)	3·9
C(3)	0·9182 (8)	0·2947 (3)	0·4347 (2)	3·8
C(4)	1·0643 (8)	0·2773 (3)	0·3902 (3)	3·6
C(5)	1·0481 (8)	0·3144 (3)	0·3312 (2)	3·6
C(6)	0·8797 (7)	0·3712 (3)	0·3191 (2)	4·0
C(7)	0·5571 (7)	0·4518 (3)	0·3489 (2)	4·1
C(8)	0·2451 (7)	0·5294 (3)	0·3729 (2)	4·2
C(9)	0·1078 (7)	0·5515 (3)	0·4190 (2)	4·0
C(10)	−0·0612 (8)	0·6076 (3)	0·4058 (2)	3·7
C(11)	−0·0840 (8)	0·6384 (3)	0·3463 (2)	3·6
C(12)	0·0637 (8)	0·6126 (3)	0·3034 (2)	3·8
N(1)	0·4136 (6)	0·4710 (2)	0·3885 (1)	5·2
N(2)	0·2286 (6)	0·5586 (2)	0·3155 (1)	4·5
O(1)	0·6051 (5)	0·3666 (2)	0·4654 (1)	5·4
H(C3)	0·933 (6)	0·272 (2)	0·479 (2)	0·44
H(C4)	1·183 (6)	0·246 (2)	0·397 (2)	0·55
H(C5)	1·155 (6)	0·303 (2)	0·296 (2)	0·35
H(C6)	0·871 (6)	0·402 (2)	0·277 (1)	0·56
H(C7)	0·562 (5)	0·478 (2)	0·305 (1)	0·61
H(C9)	0·132 (6)	0·529 (2)	0·460 (2)	0·44
H(C10)	−0·164 (6)	0·624 (2)	0·437 (2)	0·42
H(C11)	−0·202 (6)	0·676 (2)	0·338 (2)	0·51
H(C12)	0·048 (6)	0·630 (2)	0·254 (2)	0·45
H(O1)	0·503 (6)	0·406 (2)	0·454 (2)	0·34

to relative structure amplitudes by application of the usual Lorentz and polarization factors.

Structure determination and refinement

The structure amplitudes were converted to normalized values with approximate scale and temperature factors determined by Wilson's (1942) method. All structures were solved by iteratively applying Sayre's equation with the program written by Long (1965).

Table 2 gives a summary of the structure determination and refinement. The procedure was similar for all four structures. E maps based on the determined signs revealed the positions of all non-hydrogen atoms in all cases. After unit weight, full-matrix least-squares refinement (Busing, Martin & Levy, 1962) of the scale, positional parameters and isotropic temperature factors, difference maps revealed the positions of all H atoms which were assigned isotropic temperature factors 1·25 Å^2 greater than those of the C or O atoms to which they are bonded. Anisotropic refinement was continued until the parameter shifts were insignificant compared to their e.s.d.'s.

The scattering factors of Doyle & Turner (1968) were used for the non-hydrogen and of Stewart, Davidson & Simpson (1965) for the H atoms. For N-(5-bromosalicylidene)-2-aminopyridine (III) anomalous scattering factors were used for the Br atom taken from *International Tables for X-ray Crystallography* (1974).

In a final difference map maximum and minimum residual densities were insignificant compared to the average peak heights of the C atoms (Table 2). R is given by $\sum ||F_o| - |F_c||/\sum |F_o|$.

Results and discussion

The final atomic parameters and peak heights are listed in Tables 3, 4, 5 and 6 for (I), (II), (III) and (IV) respectively.* Fig. 1 shows bond distances, not corrected for thermal motion, and atom notation; Fig. 2 shows bond angles. Best least-squares planes were calculated for all molecules; deviations from these planes are listed in Table 7. Best least-squares·planes were also computed for the phenyl rings (plane A), pyridine rings (plane B) and the planes through C(1), C(2), C(7), O(1), N(1) (plane C) as shown in Table 8. The angles between the normals to the A, B, C planes are listed in Table 9.

The bond lengths of the salicylidene rings in all four molecules are in agreement with the corresponding

---

bond lengths of salicylic acid (Sundaralingam & Jensen, 1965). The tendency to shortening of C(6)—C(5) and C(4)—C(3) can be explained by a quinoid resonance structure contribution (Cochran, 1953). This is probably enhanced by the formation of the strong intramolecular hydrogen bond O(1)—H(O1)$\cdots$N(1) and the subsequent acquisition of partial keto character of the C(2)—O(1) group. A natural criterion for hydrogen bonding between the groups X—H and Y is considered to be that the distance H$\cdots Y$ should be shorter than the van der Waals approach, $d_{Y \cdots H} < r_H + r_Y$ (Olovsson & Jönsson, 1976). With $r_N = 1 \cdot 50$ (Pauling, 1960) and $r_H = 1 \cdot 0$ Å (Baur, 1972) we obtain $d_{N \cdots H} < 2 \cdot 5$ Å for possible hydrogen bonding. In the present case the mean $d_{N \cdots H}$ over the four different species is $1 \cdot 95$ Å.

The pyridine-ring distances and angles are compatible with those of pyridine (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958) and 4-(2,4-dinitrobenzyl)-pyridine (Ottersen & Seff, 1974). The equality of the exocyclic C(7)—N(1) distance, $1 \cdot 28$ Å, in all four molecules irrespective of their substituents, is remarkable. C=N distances ranging from $1 \cdot 237$ to $1 \cdot 281$ Å have been observed in a variety of differently

Table 5. *Positional parameters and peak heights for* (III) *with e.s.d.'s in parentheses*

	x	y	z	Peak height (e Å^{-3})
C(1)	0·2878 (19)	0·4461 (9)	0·8985 (21)	4·9
C(2)	0·3929 (19)	0·3876 (9)	1·0079 (20)	4·6
C(3)	0·4459 (20)	0·3271 (10)	0·9437 (22)	4·4
C(4)	0·3898 (22)	0·3247 (10)	0·7681 (24)	4·0
C(5)	0·2758 (19)	0·3847 (9)	0·6491 (23)	4·0
C(6)	0·2354 (19)	0·4445 (9)	0·7229 (21)	4·8
C(7)	0·2315 (18)	0·5134 (10)	0·9632 (21)	4·5
C(8)	0·2089 (19)	0·5823 (9)	1·1743 (21)	4·5
C(9)	0·2678 (21)	0·5876 (9)	1·3444 (23)	4·3
C(10)	0·2154 (22)	0·6515 (11)	1·4001 (22)	4·0
C(11)	0·0967 (21)	0·7056 (10)	1·2813 (23)	4·5
C(12)	0·0422 (21)	0·6938 (10)	1·1118 (23)	4·5
N(1)	0·2671 (16)	0·5174 (8)	1·1200 (17)	6·0
N(2)	0·0936 (17)	0·6317 (8)	1·0543 (18)	5·3
O(1)	0·4446 (15)	0·3867 (7)	1·1765 (14)	6·1
Br	0·2056 (2)	0·3802 (1)	0·4218 (2)	31·0
H(C3)	0·483 (17)	0·273 (7)	1·007 (16)	0·37
H(C4)	0·433 (18)	0·280 (7)	0·726 (17)	0·36
H(C6)	0·152 (16)	0·485 (7)	0·648 (15)	0·46
H(C7)	0·158 (16)	0·549 (7)	0·874 (15)	0·43
H(C9)	0·333 (17)	0·537 (7)	1·420 (16)	0·36
H(C10)	0·271 (18)	0·656 (7)	1·530 (16)	0·55
H(C11)	0·061 (18)	0·760 (7)	1·313 (16)	0·42
H(C12)	−0·040 (19)	0·738 (8)	1·002 (18)	0·37
H(O1)	0·387 (19)	0·431 (8)	1·188 (17)	0·47

Table 4. *Positional parameters and peak heights for* (II) *with e.s.d.'s in parentheses*

	x	y	z	Peak height (e Å^{-3})
C(1)	0·2846 (11)	0·4380 (5)	0·3429 (3)	4·9
C(2)	*0·2746 (12)*	*0·3939 (6)*	*0·3896 (3)*	*4·9*
C(3)	0·1112 (11)	0·3358 (6)	0·4004 (3)	4·8
C(4)	−0·0322 (11)	0·3210 (6)	0·3632 (4)	4·3
C(5)	−0·0186 (12)	0·3657 (6)	0·3154 (4)	5·0
C(6)	0·1342 (12)	0·4255 (6)	0·3048 (3)	4·7
C(7)	0·4513 (12)	0·5004 (6)	0·3320 (3)	4·3
C(8)	0·7529 (12)	0·5756 (5)	0·3512 (3)	4·9
C(9)	0·8935 (12)	0·5927 (6)	0·3897 (3)	4·5
C(10)	1·0418 (12)	0·6548 (6)	0·3773 (4)	4·1
C(11)	1·0462 (13)	0·6917 (6)	0·3285 (4)	4·2
C(12)	0·9030 (13)	0·6675 (6)	0·2916 (4)	4·4
C(13)	−0·0475 (14)	0·2361 (8)	0·4612 (4)	3·6
C(14)	0·8867 (13)	0·5486 (6)	0·4418 (3)	4·2
N(1)	0·5924 (9)	0·5144 (4)	0·3648 (3)	5·7
N(2)	0·7555 (10)	0·6096 (5)	0·3031 (3)	5·5
O(1)	0·4149 (8)	0·4037 (4)	0·4269 (2)	6·6
O(2)	0·1136 (7)	0·2969 (4)	0·4484 (2)	6·1
H(C4)	−0·110 (10)	0·269 (4)	0·369 (2)	0·39
H(C5)	−0·108 (10)	0·350 (4)	0·288 (2)	0·46
H(C6)	0·143 (10)	0·462 (4)	0·270 (2)	0·43
H(C7)	0·441 (10)	0·528 (4)	0·300 (2)	0·44
H(C10)	1·136 (11)	0·678 (5)	0·402 (3)	0·48
H(C11)	1·126 (11)	0·736 (5)	0·322 (3)	0·50
H(C12)	0·895 (11)	0·690 (4)	0·248 (3)	0·43
H(O1)	0·431 (11)	0·443 (5)	0·434 (3)	0·35
H1(C13)	−0·015 (14)	0·179 (6)	0·429 (3)	0·34
H2(C13)	−0·025 (14)	0·238 (6)	0·506 (4)	0·32
H3(C13)	−0·158 (14)	0·276 (6)	0·462 (3)	0·31
H1(C14)	0·893 (12)	0·473 (6)	0·435 (3)	0·41
H2(C14)	0·805 (13)	0·559 (6)	0·460 (3)	0·41
H3(C14)	0·964 (13)	0·575 (6)	0·465 (3)	0·44

Table 6. *Positional parameters and peak heights for* (IV) *with e.s.d.'s in parentheses*

	x	y	z	Peak height (e Å^{-3})
C(1)	0·6878 (8)	0·2754 (6)	0·6069 (2)	5·2
C(2)	0·9017 (9)	0·3758 (6)	0·6044 (2)	5·0
C(3)	1·0298 (9)	0·4162 (7)	0·6481 (2)	4·6
C(4)	0·9512 (9)	0·3595 (7)	0·6923 (2)	4·4
C(5)	0·7451 (9)	0·2563 (6)	0·6947 (2)	4·6
C(6)	0·6162 (8)	0·2190 (6)	0·6522 (2)	5·3
C(7)	0·5425 (8)	0·2352 (6)	0·5628 (2)	5·5
C(8)	0·4477 (9)	0·2397 (6)	0·4785 (2)	5·6
C(9)	0·5185 (9)	0·2972 (7)	0·4333 (2)	4·8
C(10)	0·3727 (9)	0·2608 (7)	0·3925 (2)	4·8
C(11)	0·1637 (9)	0·1651 (6)	0·3978 (2)	5·1
C(12)	0·1109 (8)	0·1096 (6)	0·4443 (2)	5·0
C(13)	0·5042 (13)	0·0884 (8)	0·7439 (2)	4·0
N(1)	0·6011 (7)	0·2816 (5)	0·5201 (1)	6·2
N(2)	0·2491 (7)	0·1443 (5)	0·4842 (1)	6·0
O(1)	0·9845 (6)	0·4322 (5)	0·5620 (1)	6·9
O(2)	0·6963 (7)	0·2050 (5)	0·7408 (1)	6·2
Cl	−0·0306 (3)	0·1187 (2)	0·3478 (0)	16·0
H(C3)	1·182 (8)	0·500 (6)	0·647 (1)	0·44
H(C4)	1·042 (8)	0·394 (6)	0·721 (1)	0·48
H(C6)	0·475 (7)	0·146 (5)	0·653 (1)	0·56
H(C7)	0·392 (7)	0·162 (5)	0·568 (1)	0·45
H(C9)	0·672 (7)	0·373 (5)	0·432 (1)	0·46
H(C10)	0·400 (8)	0·306 (6)	0·361 (2)	0·48
H(C12)	−0·042 (7)	0·033 (5)	0·448 (1)	0·49
H(O1)	0·907 (8)	0·399 (6)	0·536 (2)	0·44
H1(C13)	0·533 (9)	−0·021 (6)	0·728 (2)	0·41
H2(C13)	0·517 (9)	0·054 (6)	0·778 (2)	0·44
H3(C13)	0·361 (9)	0·136 (6)	0·734 (2)	0·45

substituted benzylideneanilines (Bürgi & Dunitz, 1970; Bernstein & Schmidt, 1972; Bernstein, 1972; Bernstein & Izak, 1976; Nakai, Shiro, Ezumi, Sakata & Kubota, 1976; Bar & Bernstein, 1977). It seems that this invariability of the C(7)—N(1) distance in the present investigation is caused by the rather strong hydrogen

bond not present in the forementioned benzylidene-aniline systems. The perturbation of C(7)—N(1) caused by the hydrogen bonding apparently overwhelms any other perturbation due to the different substituents. Bregman, Leiserowitz & Schmidt (1964) and Bregman, Leiserowitz & Osaki (1964) reported for the C(7)—N(1) distance the values 1·270 (7) and 1·288 (4) Å in N-(5-chlorosalicylidene)aniline and 2-chloro-N-salicylideneaniline respectively.

In all four species the molecules are planar (Tables 7–9) and the pyridine ring (B) has the same orientation with respect to the rest of the molecule [N(2), always cis with respect to H(C7)]. The crystal structures of (I)–(IV) are shown in Figs. 3–6. The packing is characteristic of that of flat molecules arranged in stacks along the shortest crystal axis. The orientations of the individual molecules within the stacks are not the same but the interplanar distances are similar: 3·50 for (I) and (II), 3·42 and 3·43 Å for (III) and (IV) respectively.

Table 7. *Deviations (Å) from least-squares planes*

	(I)	(II)	(III)	(IV)
C(1)	0·00	−0·01	0·02	0·02
C(2)	−0·03	0·02	−0·01	0·01
C(3)	−0·02	−0·00	−0·01	−0·04
C(4)	0·01	−0·00	0·00	−0·06
C(5)	0·03	−0·02	0·01	0·00
C(6)	0·03	−0·06	0·06	0·01
C(7)	0·04	−0·02	0·06	0·02
C(8)	0·01	0·02	−0·01	0·01
C(9)	0·07	−0·03	0·04	0·01
C(10)	0·06	−0·09	0·09	−0·04
C(11)	−0·02	−0·04	0·02	−0·05
C(12)	−0·07	0·06	−0·06	−0·01
N(1)	0·01	0·02	−0·04	0·04
N(2)	−0·06	0·09	−0·10	0·03
O(1)	−0·08	0·07	−0·07	0·04
	σ = ±0·05	σ = ±0·04	σ = ±0·05	σ = ±0·03

Table 8. *Deviations (Å) from least-squares planes A, B and C*

	(I)	(II)	(III)	(IV)
Plane A				
C(1)	0·006	0·004	−0·007	−0·007
C(2)	−0·008	0·012	−0·009	0·008
C(3)	0·004	−0·016	0·012	0·001
C(4)	0·004	0·004	0·001	−0·013
C(5)	−0·007	0·012	−0·018	0·015
C(6)	0·002	−0·017	0·021	−0·005
	σ = ±0·006	σ = ±0·012	σ = ±0·013	σ = ±0·009
Plane B				
C(8)	−0·003	−0·017	0·018	0·014
C(9)	0·000	0·019	−0·018	−0·011
C(10)	0·004	−0·006	0·012	0·000
C(11)	−0·004	−0·009	−0·006	0·006
C(12)	0·001	0·011	0·004	−0·003
N(2)	0·003	0·002	−0·010	−0·007
	σ = ±0·004	σ = ±0·015	σ = ±0·018	σ = ±0·010
Plane C				
O(1)	−0·003	0·001	0·006	−0·004
C(2)	0·006	−0·004	0·001	0·010
C(1)	−0·006	0·005	−0·016	−0·011
C(7)	0·003	−0·004	0·024	0·008
N(1)	0·000	0·002	−0·016	−0·002
	σ = ±0·007	σ = ±0·005	σ = ±0·024	σ = ±0·012

Table 9. *Dihedral angles (°)*

|	(I)	(II)	(III)	(IV)
Between A and B	4·6	4·4	4·6	−3·1
Between A and C	1·2	0·8	1·9	−1·5
Between B and C	5·5	5·2	6·3	2·2
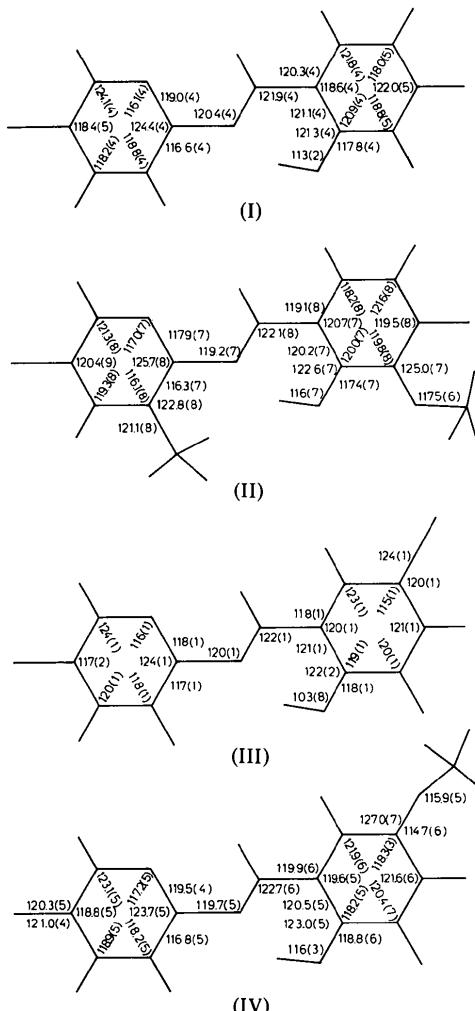
Fig. 2. Bond angles (°) for (I)–(IV). E.s.d.'s in parentheses.

In an attempt to rationalize the particular planar geometry observed, the CNDO/2 method (Pople & Beveridge, 1970) has been applied to salicylidene-2-aminopyridine (I). We have computed the energy at eight points in the three-dimensional conformational space, defined by the three rotation angles φ, χ and θ (Fig. 7). All other angles and bond distances were kept fixed at idealized values based on the structure analysis and shown in Fig. 7. All bond distances in the pyridine ring were taken equal to 1·37 Å and those of the phenyl ring equal to 1·39 Å. In addition, bond angles were fixed at 120°, except for C(2)—O(1)—H(O1) which was taken as 113°. The conformational results are collected in
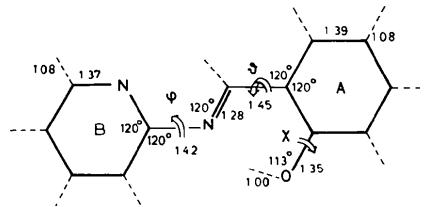
Fig. 7. Bond distances (Å), angles (°) and rotational parameters (φ,χ,θ) used in the CNDO/2 method.

Table 10. *Conformational energies of salicylidene-2-aminopyridine calculated by the CNDO/2 method*

$-E$ (kcal mol^{-1})	φ (°)	θ (°)	χ (°)
84418·6	0	0	0
84419·5	90	0	0
84417·9	135	0	0
84413·3	180	0	0
84411·7	0	90	0
84410·5	0	180	0
84406·8	0	0	90
84410·4	0	0	180
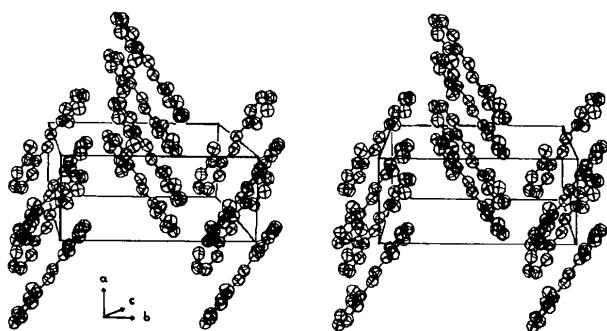
Fig. 3. *ORTEP* diagram of (I) illustrating the packing.
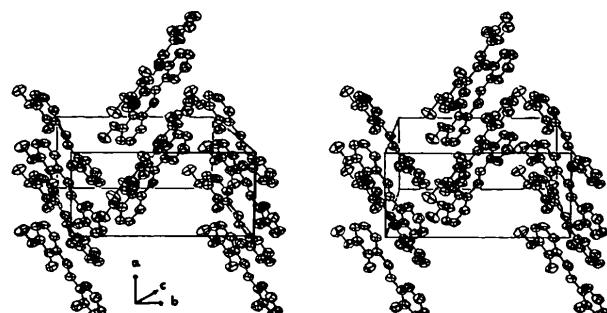
Fig. 4. *ORTEP* diagram of (II) illustrating the packing.
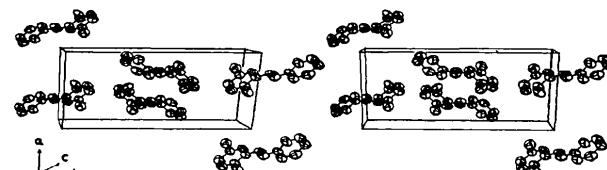
Fig. 5. *ORTEP* diagram of (III) illustrating the packing.
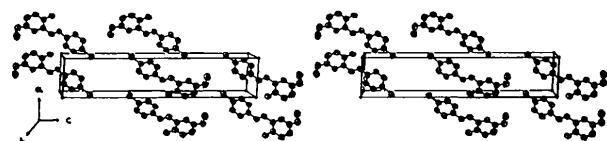
Fig. 6. *ORTEP* diagram of (IV) illustrating the packing.

Table 10. The energy barrier of 0·9 kcal mol^{-1} between the observed geometry ($\varphi = \chi = \theta = 0°$) and the one with the pyridine ring rotated by 90° ($\varphi = 90°, \chi = \theta = 0°$) corresponds to a quasi-free rotation. However, this result by itself is not significant, since the success of the CNDO/2 method to predict conformations and energy barriers of conjugated systems has been questioned (Perahia & Pullman, 1973, and references therein). In the conformation $\varphi = 180°$, $\chi = \theta = 0°$, the system is less stable by about 6 kcal mol^{-1} from the above conformations $\varphi = \chi = \theta = 0°$ and $\varphi = 90°, \chi = \theta = 0°$. This destabilization arises from steric hindrance due to the contact of H(C9) of the pyridine ring and the exocyclic H(C7). Variation of the χ angle shows that the $\chi = 0°$ is the most stable conformer, the stabilization of ~7 kcal mol^{-1} being caused mainly by the intramolecular hydrogen bond of the hydroxyl group and the imino N atom.

In conclusion, it can be said that the driving force, besides crystal forces, for the observed planarity of (I) and by the same reasoning of (II), (III) and (IV) is the intramolecular hydrogen bond which locks the salicyl-ideneimine group in the planar configuration and, in addition, the presence of the N of the pyridine moiety which does not interact repulsively with H(7) as in the salicylideneanilines.

References

BAK, B., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1958). *J. Mol. Spectrosc.* **2**, 361–368.

BAR, I. & BERNSTEIN, J. (1977). *Acta Cryst.* B**33**, 1738–1744.

BAUR, W. H. (1972). *Acta Cryst.* B**28**, 1456–1465.

BERNSTEIN, J. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 946–950.

BERNSTEIN, J. & IZAK, I. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 429–434.

BERNSTEIN, J. & SCHMIDT, G. M. J. (1972). *J. Chem. Soc. Perkin Trans.* 2, pp. 951–955.

BREGMAN, J., LEISEROWITZ, L. & OSAKI, K. (1964). *J. Chem. Soc.* pp. 2086–2100.

BREGMAN, J., LEISEROWITZ, L. & SCHMIDT, G. M. J. (1964). *J. Chem. Soc.* pp. 2068–2085.

BÜRGI, H. B. & DUNITZ, J. D. (1970). *Helv. Chim. Acta,* **53**, 1747–1764.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

COCHRAN, W. (1953). *Acta Cryst.* **6**, 260–268.

COHEN, M. D., SCHMIDT, G. M. J. & FLAVIAN, S. (1964). *J. Chem. Soc.* pp. 2041–2051.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

HADJOUDIS, E. & XEXAKIS, J. (1976). Abstr. 6th IUPAC Symp. Photochem. July 19–23, 1976, Aix-en Provence, France, pp. 121–124.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

LONG, R. E. (1965). PhD Thesis. Univ. of California, Los Angeles.

NAKAI, H., SHIRO, M., EZUMI, K., SAKATA, S. & KUBOTA, T. (1976). *Acta Cryst.* B**32**, 1827–1833.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

OLOVSSON, I. & JÖNSSON, P.-G. (1976). *The Hydrogen Bond.* Edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, Vol. II, pp. 401–402. Amsterdam: North-Holland.

OTTERSEN, T. & SEFF, K. (1974). *Acta Cryst.* B**30**, 955–959.

PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd ed., p. 260. Ithaca: Cornel Univ. Press.

PERAHIA, D. & PULLMAN, A. (1973). *Chem. Phys. Lett.* **19**, 73–75.

POPLE, J. A. & BEVERIDGE, D. L. (1970). *Approximate Molecular Orbital Theory.* New York: McGraw-Hill.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUNDARALINGAM, M. & JENSEN, L. H. (1965). *Acta Cryst.* **18**, 1053–1058.

VANDLEN, R. L. & TULINSKY, A. (1971). *Acta Cryst.* B**27**, 437–442.

VOGEL, A. I. (1966). *Practical Organic Chemistry,* pp. 653–654. London: Longmans.

WILSON, A. J. C. (1942). *Nature (London),* **150**, 151–152.

WYCKOFF, H. W., DOSCHER, M., TSERNOGLOU, D., INAGAMI, T., JOHNSON, L. N., HARDMAN, K. D., ALLEWEL, N. M., KELLY, D. M. & RICHARDS, F. M. (1967). *J. Mol. Biol.* **27**, 563–578.

Two Crystal Structures of a Cyclic Diacetylene, C21H14O4

BY V. ENKELMANN AND H. J. GRAF

Institut für Makromolekulare Chemie der Universität Freiburg, Stefan Meier-Strasse 31, D-7800 Freiburg, Federal Republic of Germany

o,o'-Diacetylenyldiphenyl glutarate (BPG) [systemic name: 16,17,18,19-tetradehydro-8,9-dihydro-6*H*-dibenzo[*h,n*][1,7]dioxacyclopentadecin-6,10(7H)-dione] crystallizes in two modifications. Modification 1 is monoclinic, $C2/c$, $a = 22.66$ (10), $b = 7.88$ (2), $c = 9.85$ (5) Å, $\beta = 108.0(5)°$, $D_x = 1.31$ Mg m^{-3} (at 120 K), $Z = 8$. Modification 2 is monoclinic, $P2_1/n$, $a = 21.680$ (20), $b = 13.830$ (9), $c = 5.420$ (2) Å, $\beta = 90.17$ (6)°, $D_x = 1.35$ Mg m^{-3}, $Z = 4$. The structures have been refined to $R = 0.078$ (752 observed reflections) and 0.062 (2982 observed reflections) for modifications 1 and 2, respectively. The different reactivity in the solid state of the two forms can be explained by the different packing of the diacetylene groups.

Introduction

Many substituted diacetylenes undergo solid-state polymerization by 1:4 addition of adjacent molecules (Wegner, 1972). Topochemical polymerization is initiated by annealing or exposure to UV, X-rays or γ-rays and leads to polymers containing fully conjugated polymer chains. In this way large, nearly defect-free polymer single crystals can be obtained. The solid-state reactivity has been found to depend only on the packing of the monomer molecules and not on the chemical nature of the substituents. The title com-