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The D. C. Conductivities of Some N-Salicylideneanilines

M. D. Cohen [a] & E. Hadjoudis [a]
[a] Department of X-ray Crystallography, The Weizmann Institute of Science, Rehovoth, Israel

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The D. C. Conductivities of Some *N*-Salicylideneanilines

M. D. COHEN and E. HADJOUDIS
Department of X-ray Crystallography,
The Weizmann Institute of Science, Rehovoth, Israel

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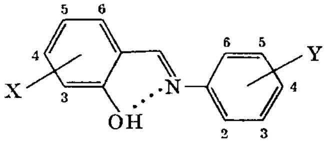
Abstract—A good deal of spectroscopic and structural data are now available on crystalline *N*-salicylideneanilines. The crystals fall into two groups which are markedly different in both molecular and crystal structures, on the one hand, and in photochemical and spectroscopic properties, on the other. It was considered that these differences should be reflected in a difference in the conduction characteristics of the two groups.

A number of members of each group were selected for this study. Conductivity measurements were performed on single crystals in different crystallographic directions. In general, all crystals studied were found to have similar specific resistivities and activation energies for conduction. However, in one case appreciably lower values of these properties were observed. This is believed to be due to suitable orientation of the molecules with respect to the crystal faces to which the electrodes were attached. Overlap calculations for this system are described in an Appendix, and the factors responsible for the observed anisotropy are discussed.

Introduction

This Laboratory has studied extensively the properties of the crystalline *N*-salicylideneanilines (I). These materials were of



(I)

interest to us, primarily, in relation to the phenomena of photochromism and thermochromism, i.e. reversible color changes induced by light and heat, respectively. Some of our observations on these phenomena have been published.[1, 2] It has been found that crystals of these compounds can be classified into two types on the basis of their spectroscopic properties (see Table 1).

It is to be stressed that this classification refers to the various compounds in given crystal structures. Thus, both compounds given as examples in Table 1 are dimorphic, with the metastable and stable forms of different types;[3] the classification given in the table refers to the modifications which are the stable ones at room temperature and above. This will be the practice throughout the paper.

TABLE 1 Classification of Crystalline *N*-Salicylideneanilines

	Type α	Type β
Effect of UV light	reversible coloration; no fluorescence	no coloration; fluorescence
Effect of heat	no coloration	reversible coloration
Name	photochromic	thermochromic
Example[a]	X = H; Y = 2-Cl	X = H; Y = 4-Cl

[a] See text in connection with dimorphism.

In addition to the above "spectroscopic" approach, structural studies have been carried out on a number of these materials. Two full three-dimensional analyses have been performed;[4, 5] another structure has been solved by analysis of two zones;[6, 7] a further structure has been analysed in projection only;[8, 9] and, finally, in many cases the space group and cell dimensions of other *N*-salicylideneanilines[2] allow reliable conjecture regarding the molecular and crystal structures involved. From this information it has been concluded that there is a general distinction between the structures of crystals of types α and β: in the thermochromic crystals the molecules are planar and pack face-to-face with short intermolecular contacts (of the order of 3.3 Å) normal to the molecular planes; in the photochromic crystals the salicylaldimino-part of the molecule is planar, but the aniline-ring lies 40 to 50° out of this plane, and the resulting structure is relatively open with no close face-to-face contacts of the molecules. In keeping with these conclusions is the observation that the photochromic forms of salicylidene-*N*-4-chloro- and -4-bromoaniline are about 10 % less dense than the corresponding thermochromic forms.[3]

Our interpretation of the phenomenon of thermochromism is as follows: there is a temperature-sensitive equilibrium in the crystal between the two tautomers of the molecule—the one with the chelating hydrogen covalently bonded to the oxygen (the "OH-form"), and the NH-form with the hydrogen bonded to the nitrogen. The NH-form absorbs at longer wavelengths; raising the temperature increases the population of this form and thus causes a deepening of color. The intramolecular hydrogen-transfer can occur in either the ground- or excited-electronic state. In contrast, a high energy is required for hydrogen transfer in the ground-electronic state of molecules in photochromic crystals; as a result no absorption attributable to the NH-form is observed. Hydrogen transfer can occur, however, in the excited-electronic state, and the crystal structure is sufficiently open to permit a subsequent geometric isomerization which leads to the colored photo-product.

Two other introductory points are to be made: first, there is evidence that all these molecules have a non-planar configuration in solution;[10] the planarity of the molecules in thermochromic crystals, as also the relatively low energy of their NH-form in these crystals, must therefore be attributed to intermolecular forces; second, it has been shown that the thermochromic absorption band is polarized in the molecular plane, and it is thus probably not due to an intermolecular charge-transfer transition.[7]

We thus have two types of crystals the properties of which can be summarized as follows: type α, non-planar molecules, open structures, no measurable concentration of NH-form; type β, planar molecules, close packed, marked intermolecular interactions, temperature-dependent concentration of NH-form. It appeared of interest to us to investigate how these distinctions would be reflected in the conduction properties. In this paper we report on the conductivities of several compounds of each type.

Other investigations of the conductivities of these materials have been published.[11, 12, 13] We will refer to their results in the Discussion.

Experimental

The compounds were prepared by conventional methods. They were purified by repeated recrystallization from suitable solvents, followed by chromatography and/or zone refining. We have no index of the purity of the materials. Most compounds were measured as single crystals only, two were measured both as single crystals and as polycrystalline films, and one as a film only. The films were prepared by crystallizing the material from the melt between two conducting-glass flats. Single crystals were grown either by slow crystallization from solution or by slow cooling of the melt in the presence of a seed crystal. Our results showed no sensitivity to the method used for crystal growth. Typically crystals used for this measurement were near cubic with edge-lengths of about 1 mm. Crystals were selected by microscopic examination, specimens showing signs of faults being rejected; all crystals used showed sharp extinction between crossed Nicols. Crystal axes were identified and alignment accomplished by means of X-ray precession photographs.

The specimens were mounted for measurement in a grounded metal box. The film-specimens were held between spring-loaded Teflon discs; the single crystals were generally silver-glued to copper-wire leads which were fixed to a glass slide by epoxy resin, for rigidity. Silver-glued samples were not measured within 2 days of application of the glue. Electrodes were attached to opposite faces of the crystal, in a sandwich arrangement, with the aim of measuring bulk-conductivity. All measurements, unless otherwise stated, were made with the sample in a slow stream of dry nitrogen. Temperature control was achieved by preheating the nitrogen. The sample was allowed to come to thermal equilibrium before measurement was made.

In most experiments the voltage applied to the crystal was obtained from a battery of dry cells, which could be tapped at a number of points between 1.5 and 22.5 V. In a few cases a stabilized high-voltage supply was used, which provided 100 to 700 V. The current passing through the crystal was led through a standard resistor, selected from the range 10^6 to 10^{11} Ω, and the voltage developed across this resistor was measured with a Keithley Electrometer Amplifier (Model 603, input impedance $> 10^{14}$ Ω).

For each crystal, mounted in a specific orientation, the conductivity, σ (or resistance, R) was determined as a function of applied voltage at constant temperature, and of temperature at constant applied voltage. It will be seen that in all cases $\log \sigma$ (or $\log R$) varies linearly with reciprocal temperature. From the slopes of the corresponding plots there were obtained the activation energies for dark conduction, E_d; these are defined by the equation:

$$\sigma = \sigma_0 \exp(-E_d/kT) \quad \text{or} \quad R = R_0 \exp(E_d/kT) \qquad (1)$$

The specific resistivity, ρ, is given by RA/L where A is the electrode area and L is the distance between the electrodes.

Experiments using electrolyte-solution electrodes employed a Pope-type cell[14] which was obtained commercially.[15] The sample was mounted between the electrode chambers by means of vacuum grease applied around the central apertures. The electrode chambers were flushed out with fresh electrolyte solution between each series of experiments.

Results

In Fig. 1 we give an activation energy plot for (β)salicylidene-N-4-chloroaniline†: the points for higher temperatures were obtained without a guard ring while those for lower temperatures were obtained with a guard ring: apart from this the crystal and electrodes were identical for the two series of measurements. Since the guard ring did not appear to influence the results we believe that

† (α) or (β) before the name of a compound indicates, in this paper, the crystal type as described in Table 1.

the measured current was due to true bulk-conduction. In the other experiment reported here guard rings were not used.

Figures 2 and 3 show the variation, at several temperatures, of current with applied voltage for two specimens: single crystals of (β)salicylidene-*N*-4-chloroaniline and of (α)salicylidene-*N*-4-bromoaniline, respectively. Such linear dependence of the current on voltage was found also for all other specimens with silver-glue electrodes which we tested. In those experiments employing higher voltages linearity was maintained throughout the range (up to 700 V). In all cases currents were slightly higher in air than in nitrogen.

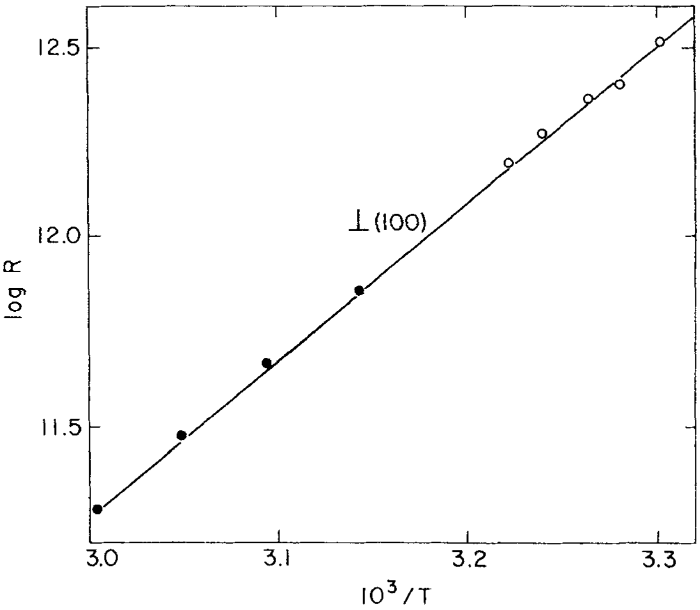


Figure 1. The dependence of the resistance of salicylidene-*N*-4-chloroaniline ⊥(100) on temperature. Open circles—with guard ring; filled circles—without guard ring.

Figures 4–6 show typical plots of $\log_{10}R$ *vs* reciprocal temperature; the various curves in a given figure all refer to the same crystal specimen. We note that for a given crystal and orientation the plot is linear, which shows the validity of Eq. (1). These plots are of interest since they demonstrate clearly the anisotropies in both the resistances and activation energies. The activation energies and room-temperature restivities for all materials tested are collected in Table 2.

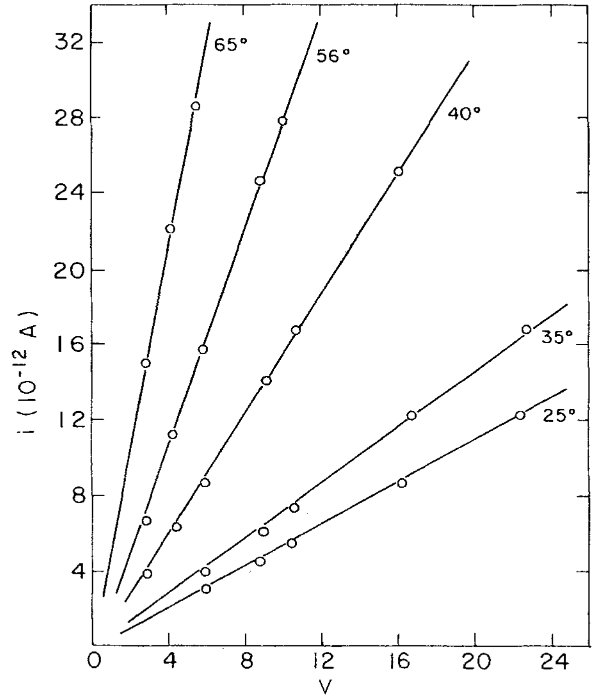


Figure 2. The dependence of the current through a single crystal of salicylidene-*N*-4-chloroaniline on applied voltage at various temperatures.

One series of experiments was performed using electrolyte-solution electrodes. A single crystal of (β)salicylidene-*N*-4-chloroaniline, 0.8 mm thick, was mounted between the electrode chambers, $(10\bar{2})$ faces being in contact with the electrodes. Initially both electrodes consisted of a 1 M aqueous solution of sodium iodide. The conductivity, in this case, was independent of the polarity of the electrodes, as expected. The dependence of the current on applied voltage is shown in Fig. 7; the non-linearity is marked.

The system was now modified in that one of the two electrode solutions consisted of 1 M aqueous sodium iodide solution saturated with iodine. The current–voltage relationship for this case is shown in Fig. 7. The symbols i_+ and i_- refer to the currents when the solution not containing the iodine is in contact with the positive and negative pole, respectively, of the external circuit.

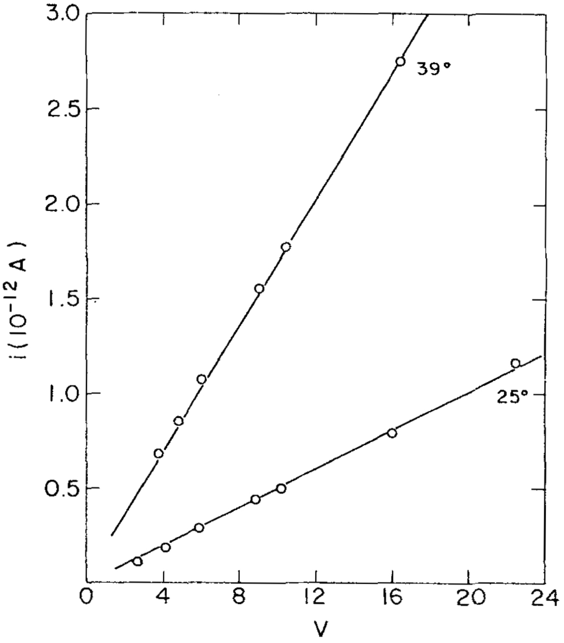


Figure 3. The dependence of the current through a single crystal of salicylidene-*N*-4-bromoaniline on applied voltage at various temperatures.

No dramatic changes are brought about by the addition of iodine. While i_+ is almost unchanged, i_- rises by about 50 % above its value in the absence of iodine. The conductivity returned to its "non-iodine" value on one or two flushings with sodium iodide solution.

Discussion

All crystals with silver-glue electrodes show ohmic behaviour in the voltage range employed. Further, in all cases the resistance dropped with the exponential of reciprocal temperature, so that the materials can be described as high-impedance semiconductors.

The use of electrolyte-solution electrodes produces pronounced curvature in the current–voltage relation, despite the low field-gradients employed. This is quite unlike the results obtained by Kallmann and Pope[16] for anthracene with sodium chloride-solution electrodes; the latter found the dark current to be ohmic up to field strengths of the order of 100,000 V cm^{-1}. There is thus an indication that in our materials there is an appreciable space-charge effect with solution electrodes. This conclusion is speculative in the absence of data on mobilities; in particular, it would not be

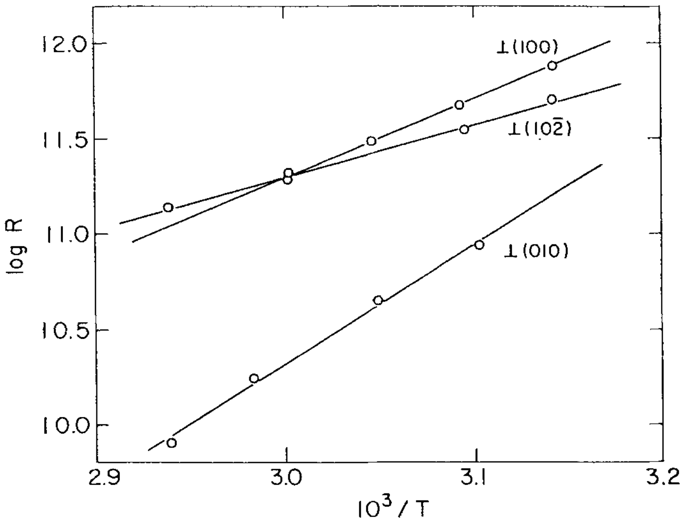


Figure 4. Activation plots for a single crystal of salicylidene-*N*-4-chloroaniline. Applied voltage 22.5.

	$\perp(100)$	$\perp(10\bar{2})$	$\perp(010)$
Electrode area (cm^2)	0.48	0.2	0.6
Thickness of crystal (cm)	0.5	0.12	0.4

TABLE 2 Conductivities of Crystalline Salicylideneanilines

Compound					E_d[b]	$\rho_{r.t.}$	
X	Y	Type[a]	Form	Direction	(eV)	(Ω cm)	Atmosphere
H	4-Cl	β	Film	—	0.99	—	Air
		β	Single Crystal	$\perp(010)$	1.15	10^{13}	Nitrogen
				$\perp(10\bar{2})$	0.53	10^{11}	,,
				$\perp(100)$	0.78	10^{12}	,,
H	4-Br	α	Single	$\perp(001)$	0.80	10^{13}	Nitrogen
H	2-Cl	α	Single Crystal	$\perp(010)$	0.99	10^{12}	Nitrogen
				$\perp(101)$	0.83	10^{13}	,,
				$\perp(\bar{1}01)$	0.83	10^{13}	,,
H	2-Br	α	Single Crystal	$\perp(010)$	0.90	10^{12}	Nitrogen
				$\perp(101)$	0.85	10^{13}	,,
5-Cl	H	β_2	Film	—	0.92	—	Nitrogen
		β_2	Single Crystal	$\perp(100)$	1.15	10^{13}	,,
				$\perp(010)$	0.99	10^{12}	,,
				$\perp(001)$	0.90	10^{13}	,,
5-Br	H	β_2	Single Crystal	$\perp(100)$	0.80	10^{13}	Nitrogen
				$\perp(010)$	0.83	10^{12}	,,
				$\perp(001)$	0.78	10^{13}	,,
3-NO_2, 5-MeO	H	β	Film	—	1.52	—	Air
				—	1.47	—	Nitrogen

[a] α-Photochromic, β-thermochromic. The subscripts refer to modifications described by Cohen, Schmidt, Flavian,[2] who give also the crystallographic data. No crystallographic data are available for the nitromethoxy compound. The structure of (β)salicylidene-N-4-chloroaniline is described briefly in the text.

[b] These values are based on E_d defined by $R = R_0 \exp(E_d/kT)$.

valid if the mobilities are high, in which case the curvature in the above plot would have to be attributed to other factors.†

The experiments with added iodine produced little change; we can probably conclude that our specimens are weak electron-donors with respect to iodine. This is in keeping with our inability to detect any charge-transfer complexes of these components in solution.[17]

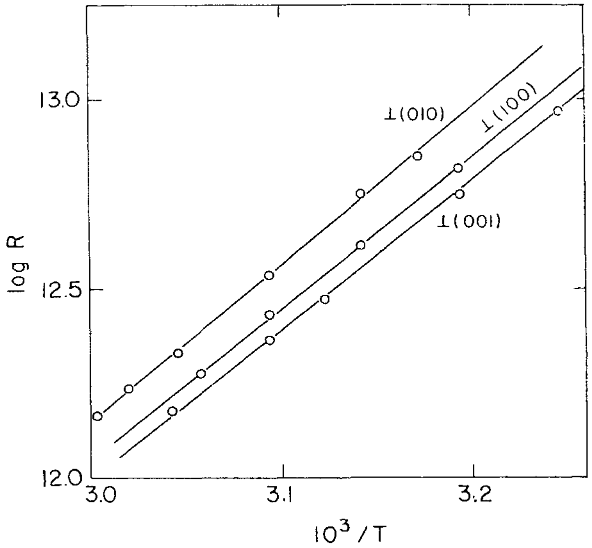


Figure 5. Activation plots for a single crystal of *N*-5-bromosalicylidene-aniline. Applied voltage 22.5.

	⊥(100)	⊥(010)	⊥(001)
Electrode area (cm^2)	0.062	0.016	0.099
Thickness of crystal (cm)	0.16	0.62	0.10

We have shown that marked structural differences exist between crystals of types α and β, and we would expect corresponding differences in the conduction behaviour. Thus, the more effective orbital-overlap in the thermochromic crystals should, presumably, lead to higher carrier mobilities in these crystals. In addition, a peculiar dependence of current on temperature might be expected

† We thank the referee for drawing our attention to this.

in the latter: at low temperatures the number of molecules in the NH-form is vanishingly small, but the number rises with increasing temperature. Thus, at high enough temperatures the conductivity would certainly be dominated by the number of NH-molecules and the conduction would be extrinsic, with the NH-molecules acting as substitutional impurities. One might therefore expect to find a discontinuity in the activation energy plots due to a change over from intrinsic to extrinsic conduction at appropriate temperatures.

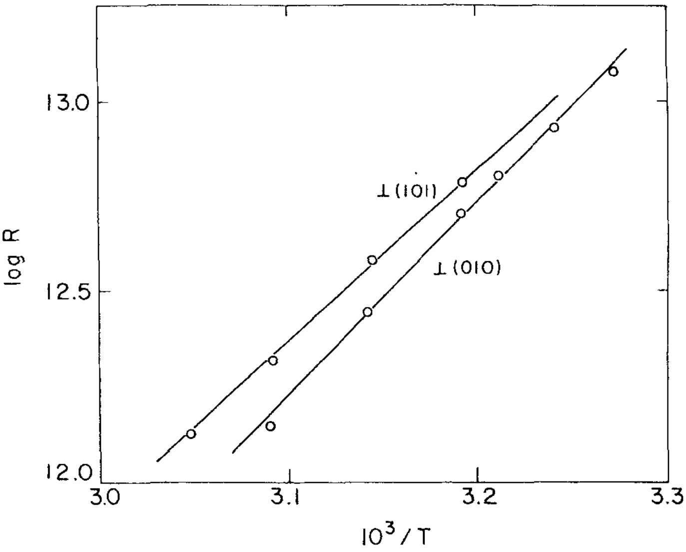


Figure 6. Activation plots for a single crystal of salicylidene-*N*-2-chloroaniline. Applied voltage 22.5.

	⊥(101)	⊥(010)
Electrode area (cm^2)	0.098	0.022
Thickness of crystal (cm)	0.14	0.70

(Such discontinuities have been demonstrated for doped anthracene by Northrop and Simpson;[18] however, in their samples the impurity concentration was independent of temperature, and the change was from extrinsic to intrinsic conduction with increasing temperature.)

A glance at the results shows no discontinuities in the activation plots, nor any marked differences between most thermochromic and photochromic compounds.† The question thus arises whether what we have measured is, indeed, a structurally sensitive property. We believe that this is so. Our argument is twofold: first, because of the Boltzmann-type dependence of the number of NH-molecules on the temperature, we should not, in fact, observe discontinuities; second, in the one compound of known structure which has marked packing anisotropy with respect to the well-developed crystal faces, we find also marked anisotropy in our conductivity data.

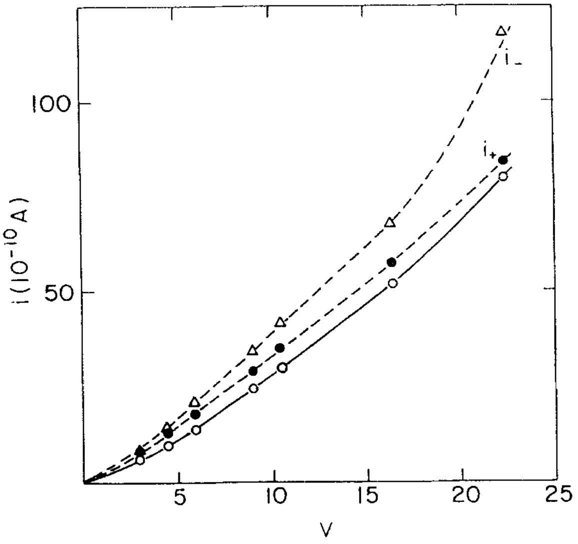


Figure 7. Dependence of the current through a single crystal of salicylidene-*N*-4-chloroaniline on applied voltage. Full curve—aqueous sodium iodide electrodes; broken curves—one electrode solution saturated with iodine. For details, see text.

To treat first the question of carrier population as a function of temperature (and thus the slopes in the activation plots), if

$$n_C = n_{NH} \exp(-E_i/kT),$$

---

† The conductivity parameters are similar to those of *trans*-stilbene,[19] for example.

where E_i is the activation energy for impurity-controlled conduction, and if

$$n_{\mathrm{NH}} = n_{\mathrm{Xtal}} \exp(-\Delta H/kT),$$

where ΔH is the enthalpy difference between the two tautomers, and n_{C}, n_{NH}, and n_{Xtal} are number densities of carriers, NH-tautomers, and of all molecules, respectively, then

$$\begin{aligned} n_{\mathrm{C}} &= n_{\mathrm{Xtal}} \exp(-E_i - \Delta H)/kT \\ &= n_{\mathrm{Xtal}} \exp(-E_i'/kT). \end{aligned}$$

The exponential dependence of the population of NH-molecules on reciprocal temperature has been demonstrated experimentally,[2] although absolute concentrations of this species have not been determined. Thus, the overall dependence of carrier population on temperature as predicted with the assumed model leads to conductivity behaviour as empirically found [Eq. (1)], but with a different apparent activation energy; no discontinuity in the corresponding plot would appear. If the molecules of both forms give rise to the same carriers, then one could go further and conclude that E_i' equals E_d, the activation energy for intrinsic conduction. This would lead to the curious conclusion that the conduction would be impurity controlled, but with activation energy that of intrinsic conduction.

We turn now to the question of the anisotropy in the conductivity of (β)salicylidene-*N*-4-chloroaniline and ask whether this is interpretable in terms of the crystal structure. The crystal data for this material are:[2] space group $P2_1/c$ with $a = 13.6$, $b = 5.85$, $c = 14.9$ Å, and $\beta = 106°30'$. There are four molecules in the unit cell and $\rho_{\mathrm{calc}} = 1.33$. The molecules lie[6, 7] with their long axes pointing approximately 10° away from the *ac* plane and almost parallel to [201]. The short molecular axis makes an angle of approximately 30° with $(10\bar{2})$. Close van der Waal's contact occurs between molecules related by inversion centers at $(\frac{1}{2}\frac{1}{2}0)$ and $(\frac{1}{2}0\frac{1}{2})$. These centric pairs are related by a twofold screw axis. Equivalent positions in the unit cell are (x, y, z), $(-x, \frac{1}{2}+y, \frac{1}{2}-z)$, $(x, \frac{1}{2}-y, \frac{1}{2}+z)$, and $(-x, -y, -z)$. The $(10\bar{2}$ faces) are well developed. Of the whole series of compounds listed in Table 2 only this compound shows pronounced pleochromism. To allow comparison between the structural data and the observed conductivities for (β)salicylidene-*N*-4-chloroaniline we have carried out an orbital-overlap calculation which we describe in the Appendix. We note, here, only the results, namely that by far the highest carrier-mobility is that of holes approximately normal to $(10\bar{2})$. This is, in fact, the direction for which lowest values were found for the room-temperature resistivity and the activation energy.

On the above basis we conclude that we have, indeed, measured a property which is sensitive to structure and, in particular, to the structural differences between photochromic and thermochromic crystals, given suitable orientations of the conductivity ellipsoid with respect to the well-developed crystal faces. This argument obviously rests on the significance of the conduction parameters which we give in Table 2. We do not have complete duplicate data on two crystals of any material. However, we obtained for three crystals of (β)salicylidene-*N*-4-chloroaniline, from different batches of material, the following activation energies (eV):

	$\perp(10\bar{2})$	$\perp(100)$	$\perp(010)$
crystal 1 (given in Table 2)	0.53	0.78	1.15
crystal 2	0.54		
crystal 3	0.53	0.79	

(all measurements at an applied voltage of 22.5; silver-glue electrodes).

We point out one shortcoming in this argument: the results given in the Appendix are relevant to mobilities. If these, in fact, are the only source of the conduction anisotropy then the slopes of the different curves in Fig. 4 should be the same, which is far from true. We must then conclude that this simple model is not in entire agreement with our data.

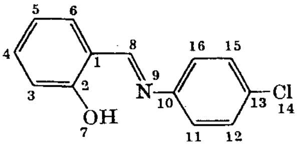
We turn, finally, to note other studies on conductivity in this series of compounds. Gallagher[11] was the first to investigate these materials; he measured the photoconductivities of a number of compounds and concluded that photochromic and thermochromic crystals differ in the times required for the build-up of the currents. This argues either for the importance of space-charge effects, or for the influence of photocoloration on photoconduction.

In two recent publications[12, 13] Gooden has reported a series of measurements on the conductivities in the dark of a series of these compounds, including some which we too have studied. The samples were pellets of powders, with silver-powder electrodes, prepared under pressure. Gooden finds a correlation between activation energies and resistivities, on the one hand, and Hamett's σ constants (for substituents in the aniline ring), on the other. This suggests that the conduction properties are quite independent of crystal structure, a conclusion which is hard to accept unless sublimation does indeed play a part in the process (which Gooden believes it does not). Our results for the same compounds disagree with Gooden's values [allowance being made for the factor of two which he includes in the exponential part of Eq. (1)], an observation which is frequently true of results for single crystals and for powders.

Appendix

We have carried out an approximate calculation of intermolecular π-electron overlap in crystalline salicylidene-*N*-4-chloroaniline; the method is essentially that of Murrell.[20] The calculation falls into two parts: the first part is a Hückel-type LCAO-MO calculation which gives the eigenvectors and eigenvalues for the isolated molecule; the second part gives the overlaps of the highest occupied and lowest unoccupied orbitals.

For the Hückel treatment each carbon atom and nitrogen was introduced bearing one p-electron, and oxygen and chlorine with two p-electrons. The Coulomb and Bond Integrals were as recommended by Streitwieser[21] (Table 3). Solution of the secular determinant gives sixteen eigenvectors and corresponding eigenvalues: the nine lower-energy MO's (ψ_1–ψ_9) are doubly occupied while the tenth is unoccupied. In Table 4 we give the coefficients of the eigenvectors for ψ_9 and ψ_{10}, the orbitals which are involved in hole and electron transfer, respectively. The numbering system for the atoms is as follows:



From the known crystal structure it was determined which pairs of atoms, belonging to different molecules, are close enough to one another to allow of significant overlap; the upper limit for "significance" was taken as 4.6 Å. There are seventy-eight pairs of atoms less than this distance apart. The overlap of the p-AO's of each such pair was obtained, taking the "direction" of the AO's as normal to the respective mean molecular planes, and making use of the method and tables given by Mulliken.[22] Slater-type AO's were employed; since the power of the exponential factor in these AO's is appreciably larger for N, O, and Cl than for C (1.95, 2.275, and 2.033, respectively, compared with 1.625) and since there are no exceptionally close contacts to these heteroatoms, all overlaps involving these atoms were neglected. Finally, from the atom-pair overlap integrals, S_{rs}, there was obtained the overlap between molecules a and b, from the relation:

TABLE 3 Parameters Used in Coulomb and Bond Integrals for Heteroatoms

Element (X)	h_X[a]	k_{CX}[b]
Nitrogen	0.5	1
Oxygen	2	0.8
Chlorine	2	0.4

[a] Coulomb integral $\alpha_X = \alpha_0 + h_X \beta_0$.
[b] Bond integral $\beta_{CX} = k_{CX} \beta_0$.

$$S_{ab} = \sum_{r,s} c_{kr} c_{ks} S_{rs}$$

Table 4 Coefficients of AO's in MO's ψ_9 and ψ_{10}

Atom No.	Coefficient of AO in MO ψ_9	ψ_{10}
1	−0.261	−0.170
2	−0.275	0.283
3	−0.014	0.120
4	0.267	−0.335
5	0.162	0.028
6	−0.177	0.323
7	0.152	−0.093
8	0.308	−0.531
9	0.431	0.404
10	−0.284	0.151
11	−0.294	−0.235
12	0.120	−0.048
13	0.361	0.256
14	−0.100	−0.042
15	0.120	−0.048
16	−0.294	−0.235

where c_{kr} and c_{ks} are the coefficients of the AO's at atoms r and s, respectively, in the kth MO.

The results of this calculation are given in Table 5; they refer to overlap for various molecules with a reference molecule (0, 0, 0)

Table 5 Molecular Overlap-Integrals for Salicylidene-*N*-4-chloroaniline. Reference molecule at (0, 0, 0), (x, y, z)

Molecule		Overlap Integral (× 10^4)	
Displacement	Symmetry coordinates	Hole (ψ_9)	Electron (ψ_{10})
(0, −1, 0)	(x, y, z)	0.32	1.20
(0, 1, 0)	(x, y, z)	0.92	0.56
(1, −1, 0)	$(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	0.86	0.88
(1, −1, 1)	$(-x, -y, -z)$	0.23	−0.31
(1, 0, 0)	$(-x, \frac{1}{2}+y, \frac{1}{2}-z)$	−0.19	0.53
(1, 0, 1)	$(-x, -y, -z)$	9.19	−0.40
(2, 0, 1)	$(-x, -y, -z)$	0.39	0.26

situated at (x, y, z). Each molecule is labelled according to its spatial relationship to this reference molecule, i.e. the number of translations in the directions a, b, and c, and the coordinates arrived at from (x, y, z) by the appropriate symmetry operations.

We see from the table that the calculation indicates that holes are more mobile than electrons, and that there is a strong preference for the direction $(0, 0, 0)$ (x, y, z)–$(1, 0, 1)$ $(-x, -y, -z)$, which is approximately normal to $(10\bar{2})$. We have discussed this apparent agreement with experiment in the main text.

It is necessary to point out the approximations in the above treatment. There is a large uncertainty attached to the best values of the Coulomb and Bond Integrals to be used for the heteroatoms in the Hückel treatment. This is aggravated, in this case, by the neglect of the influence of the hydrogen bond. Other deficiencies have been pointed out by Katz and coworkers:[23] the use of Slater-orbitals for calculation of overlap at relatively large distances is undesirable, as these orbitals strongly underestimate the values of the wave functions in that range; further, only two-center overlap terms have been used, whereas three-center terms can contribute substantially. Finally, we recall that we have considered the overlap between pairs of carbon atoms only.

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