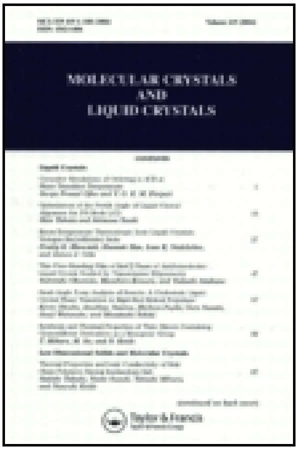

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Mesomorphism Induced by Hydrogen Bonding between Complementary Components. Crystal and Molecular Structure of the Adduct between 4-Phenylbenzoic Acid and 4-Cyano-4′-Stilbazole

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Mesomorphism Induced by Hydrogen Bonding between Complementary Components. Crystal and Molecular Structure of the Adduct between 4-Phenylbenzoic Acid and 4-Cyano-4′-Stilbazole

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Hydrogen-bonded complexes were formed between complementary, proton-donating and accepting components. Symmetric (two-to-one) complexes of 4-substituted benzoic acids and 4,4′-bipyridine and structurally unsymmetric (one-to-one) complexes of benzoic acid derivatives with either 4-cyano or 4-nitro-4′-stilbazole, were studied. Despite the fact that none of the components was particularly mesogenic, nor contained an alkyl chain, many of the resultant mixtures displayed nematic mesomorphism. In some cases the clearing temperature was above 220°C. The crystal and molecular structure of one of these liquid-crystalline complexes, **2c** (4-phenylbenzoic acid/4-cyano-4′-stilbazole) is described.

Keywords: Hydrogen bonding; stilbazoles; liquid crystals

In crystal engineering the hydrogen bond is often the dominant intermolecular interaction [1], giving an element of predictability to some aspects of the solid state structure. This hydrogen-bonded approach can also be applied to liquid crystals, where the stronger intermolecular interactions are often crucial in stabilising the mesomorphic state. It is hoped that the structural control hydrogen bonding offers to crystal engineers can be carried over to liquid-crystalline systems. Indeed the number of publications in the area of hydrogen-bonded liquid crystals over the last five years clearly reflects the increased interest in this subject [2]. Many groups have demonstrated induced mesomorphism in mixtures of complementary components. In particular many 'polymeric' materials have been examined. These include 'pseudo' main-chain structures [3], side-chain materials [4] and cross-linked polymer networks [5]. This is in addition to more established work on hydrogen-bonded mesogens in, for example, carbohydrate and diol liquid crystals, where mesomorphism appears to be promoted by extended hydrogen-bonded interactions between like molecules [2].

A relatively large number of low-molar-mass materials have also appeared in the literature. We note in particular; the first demonstration of enhanced mesomorphism by Kato and Fréchet [6], the totally induced mesomorphism in methoxystilbazole derivatives by Yu *et al.* [7], and a near room temperature nematogen consisting of only two aryl rings [8].

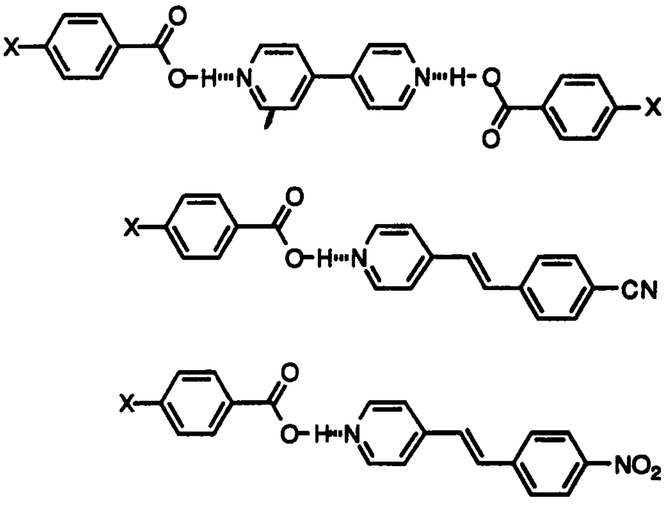
Whether hydrogen-bonded mesogens can offer useful, improved properties remains to be seen. Kato and ourselves have examined the spontaneous polarisation in some S_{C*} derivatives [9], while Griffin *et al.* [10] have studied molecular dynamics by NMR. We have recently described a material with a non-ionic, hydrogen-bonded ground state, which becomes essentially ionic in the mesophase [11]. This population of the ionic hydrogen bonded state is in excess of the normal thermal population, and is attributed to a stabilisation of the ionic state in the environment created by the structure of the phase.

In this paper we report on three new series of mesomorphic, hydrogen-bonded complexes. The behaviour of these adducts, whose proposed structures are shown in Figure 1, is in stark contrast with the non-mesogenic nature of their components. The first series are structurally symmetric and composed of 4,4'-bipyridine, hydrogen bonded to either 4-nitro, 4-cyano, 4-phenyl or 4-methylbenzoic acid in a one-to-two ratio, giving complexes **1a**, **1b**, **1c** and **1d** respectively. The two subsequent series consist of one-to-one adducts giving structurally unsymmetric mesogens, formed by complexing 4-cyano-4'-stilbazole with 4-nitro-, 4-cyano-, 4-phenyl- and 4-methylbenzoic acid, to give the adducts **2a**, **2b**, **2c** and **2d**. In the third series, 4-nitro-4'-stilbazole was complexed with 4-nitro-, 4-cyano- and 4-phenylbenzoic acids to give the complexes **3a**, **3b** and **3c**.

RESULTS AND DISCUSSION

Mesomorphism

The mesomorphism of these materials was studied by polarising optical microscopy and differential scanning calorimetry (DSC) experiments, and is



1a: X = -NO_2
1b: X = -CN
1c: X = -C_6H_5
1d: X = -CH_3

2a: X = -NO_2
2b: X = -CN
2c: X = -C_6H_5
2d: X = -CH_3

3a: X = -NO_2
3b: X = -CN
3c: X = -C_6H_5

FIGURE 1 The proposed structures of the hydrogen bonded adducts.

presented in Table I. For the symmetric series, **1**, we observed liquid crystalline behaviour for all of the complexes with the exception of **1a**, the nitro derivative. The cyano and phenyl analogues, **1b** and **1c** showed essentially similar mesomorphism, with enantiotropic nematic phases at rather high temperatures; the stability of the phase being marginally higher in the phenyl complex. We note that the entropies of transition are very similar for both adducts, and that $\Delta S_{N\text{-}I}$ is quite large, *ca.* 10 J K^{-1} mol^{-1}, which may be indicative of a large value for the order parameter, *S*, which would not be too surprising given the high aspect ratio of these complexes. The methyl derivative, **1d**, showed monotropic behaviour, although here the occurrence of a second metastable crystal polymorph gives the appearance of enantiotropic mesomorphism. In comparison with **1b** and **1c**, it is clear that although the methyl group has a positive effect in destabilising the crystal, it does not impart the same beneficial properties as the cyano and phenyl groups in stabilising the mesomorphism. It is interesting to compare the phase behaviour of **1d** with similar complexes described by Kato *et al.* [12]. Here the methyl group is replaced by butyl, pentyl and octyl homologues, giving materials with a much reduced melting point, and enantiotropic behaviour is observed. Although the nematic phase was replaced by a smectic modification in these higher homologues, the clearing temperatures at 147, 153 and 153°C respectively are remarkably similar to the value observed in **1d**.

TABLE I The mesomorphism of the complexes; transitions and thermal parameters

Complex	*Transition*	$T/^{\circ}C$	$\Delta H/kJ\,mol^{-1}$	$\Delta S/J\,K^{-1}\,mol^{-1}$
1a	K-I	198	84.6	167
1b	K-N	186	47.8	104
	N-I	206	5.15	10.9
1c	K-N	183	57.1	127
	N-I	212	4.70	9.9
1d	K-I	161	58.9	138
	(K′-N)	149	-	-
	(N-I)	153	−3.30‡	−8.0
2a	K-I	190	38.9	85
	(N-I)	189.5	−1.53‡	−3.4
2b	K-N	207		
	N-I	209	26.3§	56
2c	K-N	160	34.2	80
	N-I	222	2.2	4.5
2d	K + K′ − K + I	130		
	K + I − N	155	54.8§	129
	N-I	162	−2.71‡	−6.6
3a	K-I	208	48.1	101
3b	K-I	190	43.6	95
	(N-I)	188	−0.82‡	−1.8
3c	K-N	166	29.1	77
	N-I	221	2.31	4.8

Transition temperatures are taken from the optical microscopy; DSC thermograms were run at 10 K min^{-1}; enthalpies and entropies are taken as averages of 2nd and 3rd heating cycles; K = crystal, N = nematic and I = isotropic liquid; parenthesis indicate a monotropic phase transition; - indicates a transition not seen in the DSC experiment; ‡ signifies the value was obtained from cooling curves; § denotes combined enthalpies of transition.

In these systems the nature of the terminal substituent has a massive effect upon the mesomorphism, and different groups each bring very different properties to the mesogen. For instance, the most significant effect of the cyano group is to impart a large, local dipole to the molecule. Such a longitudinal dipole stabilises the liquid crystal phase by well-known antiparallel associations [13]. On the other hand the phenyl group stabilises the mesomorphism simply by increasing the structural and polarisability anisotropies of the molecule. The methyl group, however, adds very little to the mesomorphism and is often used primarily to destabilise the crystal phase.

Although it is not really possible to deconvolute the effects of each substituent from the effects of hydrogen bonding, certain comparisons can be made. For instance, the order of increasing melting point of the adducts is the same as in the benzoic acids themselves. We should also point out that 4-phenylbenzoic acid does in fact posses a monotropic nematic phase which clears at 211°C, some 9°C below its melting point, and indeed, the phenyl derivative **1c** has the highest nematic phase stability, although it is somewhat curious that its clearing point is only 212°C. It would appear that the addition of two aryl rings (4,4′-bipyridine) adds nothing to the stability of the mesophase, and that only the reduction in melting point that is significant. It is probable that the extra, flexibility of the hydrogen bond almost exactly counters the effect of the 4,4′-bipyridyl core.

Another comparison can be made with certain covalent analogues. In this way it may be possible to deconvolute all other effects not due to hydrogen bonding. Thus, the complex **1d** can be compared with 4,4′-biphenyldi(4″-methylbenzoate), Figure 2a, a complex studied by Karamysheva *et al.* [14]. We observed a massive destabilisation of the transition temperatures in **1d**, $T_{K\text{-}N}$ being some 87°C lower, and the clearing point, $T_{N\text{-}I}$ being 227°C lower than in this all-covalent analogue. Such a large difference is consistent with the flexibility of the hydrogen-bonded group which acts to destabilise the mesophase of the complexes with respect to their nominal covalent analogues.

An equimolar ternary mixture of 4-cyanobenzoic acid, 4,4′-bipyridine and 4-nitrobenzoic acid was prepared. This mixture was observed to melt at about 150°C to a nematic phase which cleared at 214°C. Although the melting transition was not perfectly sharp, showing evidence of biphasic

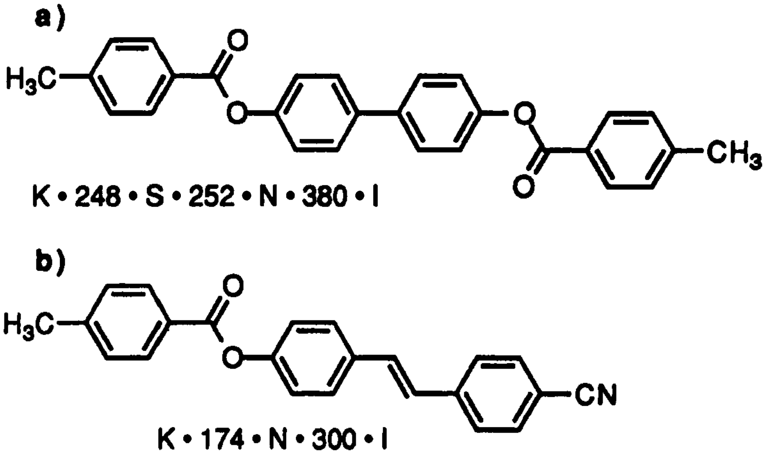


FIGURE 2 Comparable all-covalent mesogens. **a)** 4,4′-biphenyldi(4″-methylbenzoate), **b)** 4-cyanostilbene-4′-(4″-methylbenzoate).

behaviour, the clearing transition was abrupt. This would suggest that while the solid state is likely to consist of a mixture of **1b** and **1c**, the nematic and isotropic phases probably contain, a mixture of the pure adducts (**1b** and **1c**) and the one-to-one-to-one hetero complex in equilibrium. In any case, whether simple mixture or true hetero complex, the fact that the range of the nematic phase is extended to over 60°C is not diminished.

The second and third series behave similarly to the complexes described above. Mesomorphism is seen for all complexes again with the exception of the dinitro adduct, **3a**. Comparing the complexes of the 4-cyano- with the 4-nitro-4′-stilbazole, it can be seen that the cyano groups are marginally better at stabilising the mesomorphism. Thus the complex **2b**, with cyano groups at both ends, displays a narrow range of enantiotropic nematic phase, before clearing at 209°C. Changing one of the cyano groups for a nitro, we see both a destabilisation of the melting, and clearing points. This results in monotropic mesomorphism, with phases appearing just below the melting points in **2a** and **3b**. If both cyano groups are replaced by nitro groups, (**3a**) then the melting point is increased and no mesomorphism is seen at all. This apparently adverse affect of the nitro group on the mesomorphism, is not always the case. Recently we have reported on hydrogen bonded stilbazole/phenol complexes [15, 16] where the nitro derivatives significantly stabilise the nematic phase in comparison to their cyano analogues.

The behaviour of the phenyl complexes **2c** and **3c** is very similar, both in terms of transition temperatures and entropies. These derivatives show a 60°C nematic range before clearing at relatively high temperatures, in excess of 220°C. Given the non-mesogenic structures of the components, it would seem likely that any significant dissociation would destroy the mesomorphism. Thus it is probably valid to suppose that up to the high clearing temperatures, the adducts remain intact. These conclusions are supported our recent spectroscopic studies of stilbazoles with 2,4-dinitrophenol [11, 16].

The mixture of 4-cyano-4′-stilbazole and 4-methylbenzoic acid, **2d**, gave an anomalous result. Each time the same behaviour was observed regardless of the method of preparation, either from a melt synthesis or by evaporation from solutions of the components. This behaviour was observed both on heating and cooling the sample, indicating that a thermodynamic equilibrium is obtained. On heating a sample of **2d**, at 130°C about one half of the material melted to give a biphasic mixture with both crystals and an isotropic liquid. On continued heating, at about 155°C and relatively sharply, the remaining crystal phase melted or dissolved in the isotropic liquid, to give a nematic phase which persisted until 162°C. Although apparently odd such behaviour is thermodynamically allowed, simply reflecting the lower

Gibbs function for the mixture of crystals and isotropic, than for the nematic phase at temperatures below 155°C.

The behaviour is interpreted as follows. First, in the solid state, a complex is not formed, rather an intimate mixture of the two components. At 130°C the cyanostilbazole melts, giving the observed biphasic behaviour, and then at 155°C, melting or dissolution of the 4-methylbenzoic acid produces the hydrogen-bonded complex, which at these temperatures shows a nematic phase. Further heating, simply forces the clearing transition of the molecular complex to an isotropic state at 162°C. Such behaviour, where upon mixing the formation of a stronger hydrogen bond does not occur in the solid state, has been observed before. In a crystallographic study of heteroacid dimers Krishnamuhar Sharma *et al.*, report [17] that unlike other similar derivatives, mixtures of 4-(*N*, *N*-dimethylamino)benzoic acid and 3, 5-dinitrobenzoic acid did not form complementary hydrogen-bonded adducts in the solid state, the crystals consisting of a mixture of both homoacid dimers.

Although the behaviour of **2d** is anomalous, the fact that a nematic phase of the complex is seen, means that a comparison of $T_{N\text{-}I}$ with an all-covalent material has some meaning. Thus 4-cyanostilbene-4′-(4″-methylbenzoate), (Fig. **2b**) studied by Dubois *et al.* [18] shows a nematic phase from 174 to 300°C. Comparison with **2d** again illustrates the massive destabilisation that the hydrogen-bonded link brings to the mesophase, being so much more flexible. The clearing point of **2d** was some 138°C lower than the allcovalent material.

In summary, although the induction of high-temperature nematic phases from non-mesomorphic components demonstrates control of simple hydrogen-bonded systems, anomalous behaviour was observed in some of these systems.

Infrared Studies

FTIR studies of the adducts was used to show that complexation had occurred. Large changes in the bands associated with hydrogen bonding were seen in spectra of the components and the complexes. In fact, all derivatives showed similar spectra in regard to bands associated to the hydrogen bonding interaction. Thus, only the observed changes on complexation of **1c** will be described here.

The spectra of 4-phenylbenzoic acid showed a single broad band at 2950 cm^{-1} corresponding to the ν_{OH} stretch. In addition we observed Fermi resonances [19] of $2\gamma_{OH}$ and $2\delta_{OH}$ with ν_{OH} at 2669 and 2551 cm^{-1} respectively. The hydrogen bonded carbonyl was found at 1681 cm^{-1}, and the broad band at 940 cm^{-1} was attributed to the 'out-of-plane' deformation of the OH–O group. Upon complexation with 4,4'-bipyridine, we observed a 'Type I, Class b' spectrum as defined by Hadzi [20], with three broad bands, *A* at *ca.* 2900, *B* at 2450 and *C* showing two maxima at 1947 and 1890 cm^{-1}. Such a pattern was also reported by Johnson and Rumon [21] in similar carboxylic acid/pyridyl adducts. The band *A* was the least intense of the trio, and its precise maximum was obscured in part by aryl C—H stretches at 3028 cm^{-1}, and by sub-maximum in the band at 2920, 2780 and 2597 cm^{-1}. We also note the apparent loss of the 'out-of-plane' deformation mode in the complex.

In addition to the large changes associated with the OH modes, we also observed a shift in the carbonyl stretch, increasing in frequency by 9 cm^{-1} to 1690 cm^{-1}. The pyridyl ν_{CN} stretch also moved to higher wavenumber, in 4,4'-bipyridine it was at 1598 cm^{-1} and in **1c** it was found at 1604 cm^{-1}. All of these changes were in agreement with the formation of the acid/pyridyl hydrogen bonded motif.

Crystal and Molecular Structure of 2c

Crystallisation of **2c** from most solvents gave a fibrous material, unsuitable for single crystal studies. However, slow evaporation from a toluene solution yielded two habits, the fibres and colourless blocks. The single crystal structure of such a block was solved and the crystallographic data can be found in Tables II and III. Since apparently two crystal habits were formed, the blocks, the fibres and a powder sample obtained by a quick evaporation from a tetrahydrofuran solution, were all melted. No discernible difference in melting point or mesomorphism was observed.

The adduct structure, Figure 3, was entirely as expected and the pyridyl/carboxylic acid motif is the only hydrogen bonding interaction present. All interatomic distances and angles, are found to be in the normal ranges. The hydrogen bond is found to be almost linear with an N(1)H(1)O(2) angle of 179.6°. The O(2)—H(1) and N(1)—H(1) bond lengths are 1.266(9) and 1.364(9) Å respectively, showing that the hydrogen bond is nonionic, consistent with the pK_a values of the corresponding components. It also compares well with the N—H—O distance of 2.66 Å found in nicotinic acid [22].

The molecular packing in the crystal is shown in Figure 4. The crystal consists of linear, ferroelectrically aligned chains of the mesogen, such that within a chain the adducts all pointed in the same direction, and the hydrogen bonding interaction was sandwiched between the first and last aryl

TABLE II Atomic coordinates [× 10^4] equivalent isotropic displacement parameters [$Å^2$ × 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U(eq)*
N(1)	– 857(6)	2918(7)	4029(5)	77(2)
N(2)	– 14920(9)	1259(7)	– 803(7)	100(2)
O(1)	1931(6)	1212(6)	4778(5)	84(2)
O(2)	2246(5)	3317(5)	5043(5)	86(2)
C(1)	– 1386(8)	3787(8)	3537(8)	83(2)
C(2)	– 2962(8)	3665(8)	2937(7)	76(2)
C(3)	– 4121(7)	2609(8)	2802(7)	62(2)
C(4)	– 3561(8)	1731(8)	3311(7)	71(2)
C(5)	– 1942(9)	1865(8)	3906(7)	76(2)
C(6)	– 5794(8)	2521(8)	2175(7)	67(2)
C(7)	– 7037(8)	1746(8)	2131(7)	67(2)
C(8)	– 8722(7)	1633(7)	1490(6)	57(2)
C(9)	– 9227(8)	2308(7)	694(7)	71(2)
C(10)	– 10836(8)	2171(8)	91(7)	70(2)
C(11)	– 11952(7)	1397(7)	288(6)	54(2)
C(12)	– 11491(8)	708(7)	1097(7)	68(2)
C(13)	– 9871(8)	850(7)	1696(7)	66(2)
C(14)	– 13607(9)	1283(8)	– 329(7)	67(2)
C(15)	9590(7)	3199(7)	7524(7)	60(2)
C(16)	10369(8)	2247(8)	7216(7)	74(2)
C(17)	11991(10)	2422(10)	7818(9)	88(3)
C(18)	12860(9)	3603(10)	8750(9)	93(3)
C(19)	12145(9)	4587(9)	9099(9)	100(3)
C(20)	10494(9)	4377(9)	8480(8)	83(3)
C(21)	7865(7)	3005(7)	6926(6)	61(2)
C(22)	7199(7)	4002(7)	6660(7)	67(2)
C(23)	5554(8)	3791(8)	6072(7)	72(2)
C(24)	4552(7)	2583(7)	5790(6)	61(2)
C(25)	5201(8)	1595(7)	6055(7)	67(2)
C(26)	6828(9)	1779(8)	6594(7)	75(2)
C(27)	2784(8)	2323(8)	5170(7)	64(2)

groups of two adjacent adducts. That is the N—H—O interaction lies between the phenyl group of another stilbazole and a phenyl group of another 4-phenylbenzoic acid. Antiparallel alignment of cyano groups from adjacent adducts between chains, means that the ferroelectric structure is not extended to higher dimensions.

EXPERIMENTAL

General Characterisation

Components were characterised by microanalysis and NMR spectroscopy, performed by Sheffield University service. Chemicals were used as received

TABLE III Bond lengths [Å] and angles [°] for 1

N(1)—C(1)	1.332(9)	N(1)—C(5)	1.352(10)
N(2)—C(14)	1.145(9)	O(1)—C(27)	1.225(8)
O(2)—C(27)	1.288(8)	C(1)—C(2)	1.357(10)
C(2)—C(3)	1.390(10)	C(3)—C(4)	1.362(9)
C(3)—C(6)	1.449(10)	C(4)—C(5)	1.388(10)
C(6)—C(7)	1.293(11)	C(7)—C(8)	1.455(10)
C(8)—C(9)	1.383(9)	C(8)—C(13)	1.385(10)
C(9)—C(10)	1.381(10)	C(10)—C(11)	1.350(10)
C(11)—C(12)	1.399(9)	C(11)—C(14)	1.427(11)
C(12)—C(13)	1.389(10)	C(15)—C(16)	1.368(9)
C(15)—C(20)	1.396(10)	C(15)—C(21)	1.464(9)
C(16)—C(17)	1.384(11)	C(17)—C(18)	1.380(11)
C(18)—C(19)	1.366(11)	C(19)—C(20)	1.405(11)
C(21)—C(22)	1.393(9)	C(21)—C(26)	1.406(10)
C(22)—C(23)	1.394(9)	C(23)—C(24)	1.388(10)
C(24)—C(25)	1.376(9)	C(24)—C(27)	1.493(10)
C(25)—C(26)	1.377(10)		

C(1)—N(1)—C(5)	118.2(6)	N(1)—C(1)—C(2)	122.7(8)
C(1)—C(2)—C(3)	121.1(7)	C(4)—C(3)—C(2)	115.4(6)
C(4)—C(3)—C(6)	124.8(7)	C(2)—C(3)—C(6)	119.7(7)
C(3)—C(4)—C(5)	122.5(7)	N(1)—C(5)—C(4)	120.0(7)
C(7)—C(6)—C(3)	128.6(7)	C(6)—C(7)—C(8)	129.2(7)
C(9)—C(8)—C(13)	118.2(6)	C(9)—C(8)—C(7)	122.3(7)
C(13)—C(8)—C(7)	119.6(6)	C(10)—C(9)—C(8)	120.8(7)
C(11)—C(10)—C(9)	120.7(7)	C(10)—C(11)—C(12)	120.3(6)
C(10)—C(11)—C(14)	119.9(6)	C(12)—C(11)—C(14)	119.8(6)
C(13)—C(12)—C(11)	118.5(6)	C(8)—C(13)—C(12)	121.4(6)
N(2)—C(14)—C(11)	176.6(9)	C(16)—C(15)—C(20)	117.5(6)
C(16)—C(15)—C(21)	122.7(7)	C(20)—C(15)—C(21)	119.7(6)
C(15)—C(16)—C(17)	122.3(8)	C(18)—C(17)—C(16)	119.0(7)
C(19)—C(18)—C(17)	121.2(7)	C(18)—C(19)—C(20)	118.5(8)
C(15)—C(20)—C(19)	121.4(7)	C(22)—C(21)—C(26)	118.0(6)
C(22)—C(21)—C(15)	122.1(7)	C(26)—C(21)—C(15)	119.9(6)
C(21)—C(22)—C(23)	121.2(7)	C(24)—C(23)—C(22)	119.7(6)
C(25)—C(24)—C(23)	119.4(6)	C(25)—C(24)—C(27)	119.3(7)
C(23)—C(24)—C(27)	121.2(6)	C(24)—C(25)—C(26)	121.4(7)
C(25)—C(26)—C(21)	120.3(7)	O(1)—C(27)—O(2)	123.3(6)
O(1)—C(27)—C(24)	120.6(7)	O(2)—C(27)—C(24)	116.0(7)

Symmetry transformations used to generate equivalent atoms:

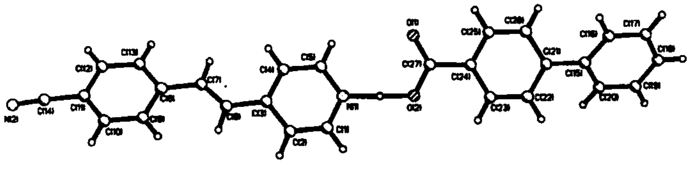


FIGURE 3 The structure of the adduct **2c**, composed of 4-cyano-4′-stilbazole and 4-phenylbenzoic acid.

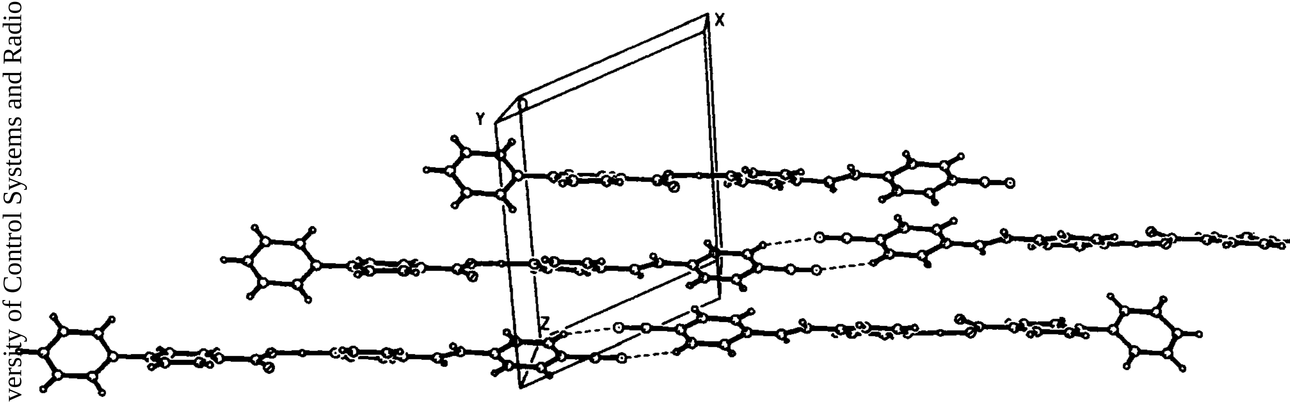


FIGURE 4 The packing arrangement and unit cell of the co-crystal **2c**.

unless otherwise stated. Infra-red spectra were obtained as KBr Discs on a Perkin-Elmer 1600 series FTIR. Proton NMR were recorded on a Brücker WM250 spectrometer and chemical shifts are quoted relative to an internal standard. δ values are given in ppm, and coupling constants are in Hz. The mesomorphism was studied by heated stage polarising optical microscopy, using a Zeiss Labpol microscope equipped with a Linkam TH600 hot-stage and a PR600 temperature controller. After phase types and transition temperatures had been established, differential scanning calorimetry was used to determine the heats of transition. For this a Perkin-Elmer DSC7 instrument and a 7000 series computer were employed.

Complex Formation

The components were dissolved in the correct molar ratios in tetrahydrofuran (freshly distilled from sodium benzophenone ketyl). After some minutes the solvent was removed under reduced pressure to give the product as a white polycrystalline powder. The compromise to purity inherent in the weighing out of the components and mixing process is estimated to be less than 1%.

Trans-4-Cyano-4′-Stilbazole

4-Bromobenzonitrile (5.01 g, 27.5 mmol), 4-vinylpyridine (3.78 g, 36.0 mmol), triethylamine (3.82 g, 37.8 mmol), hexakis(acetato)tripalladium(II) (69.3 mg, 103 μmol), tri(*ortho*-tolyl)phosphine (0.167 g, 0.550 cm^3) and acetonitrile (70 cm^3) were placed in a thick-walled, Fisher-Porter tube under an argon atmosphere. The system was sealed and heated to 120°C for 3 days at constant volume. The reaction mixture was then taken into dichloromethane (100 cm^3) and filtered through Celite®. The filtrate was washed with water (3 × 100 cm^3) and saturated sodium chloride solution (1 × 100 cm^3). The organic phase was dried over anhydrous magnesium sulphate, filtered again and the solvent removed under reduced pressure on a rotary evaporator. Heptane was added to the residue and the mixture was brought to reflux in air for 3 hours, effecting a polymerisation of the residual 4-vinylpyridine. The heptane was removed under reduced pressure and the solid was repeatedly extracted overnight into hexane with a Soxhlet apparatus. The hexane was cooled and the white precipitate collected by filtration, washed with cold hexane and then dried under high vacuum, to give the product *trans*-4-cyano-4′-stilbazole (4.74 g, 23.0 mmol, 84%); m.p. 130°C; (found: C, 81.2; H, 4.9; N, 13.5. $C_{14}H_{10}N_2$ requires: C, 81.5; H, 4.9;

N, 13.6%); γ_{max}/cm^{-1} 2223 s (ν_{CN}); δ_H (250 MHz; $CDCl_3$) 7.11 (1H, —CH:CH—, d, $^3J_{HH} = 16.5$ Hz), 7.29 (1H, —CH:CH—,d), 7.40 (2H, pyridyl, AA'XX', J = 6.7 Hz), 7.64 (4H,—C_6H_4—, AA'BB') and 8.62 (2H, pyridyl, AA'XX').

4-Nitro-4'-stilbazole was synthesised by Dr A. Thornton in an analogous procedure to the synthesis of the cyano derivative [23]. 4-Phenylbenzoic acid was synthesised by Mr J. P. Broad from the 4-cyanobiphenyl by standard procedures. All other components were received from commercial sources.

Single Crystal Structure Determination

A single crystal of **2c** (4-cyano-4'-stilbazole/4-phenylbenzoic acid) was selected and the three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 40°$ on a Siemens P4 diffractometer by the omega scan method. Of the 1854 reflections measured, all of which were corrected for Lorentz and polarisation effects (but not for absorption), 940 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods and refined by full matrix least squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode with the exception of H1 (the hydrogen-bonded proton) which was detected by the use of a low-theta difference map. It was then also refined in riding mode. Refinement converged at a final $R = 0.0626$ ($wR_2 = 0.3022$ for all 1357 unique data, 280 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -0.171 and 0.166e $Å^{-3}$. A weighting scheme $w = 1/[\sigma^2(Fo^2) + (0.0987 \ {*P})^2 + 1.6419{*P}]$ where $P = (F_0^2 + 2{*}F_c^2)/3$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93 [24] as implemented on the Viglen 486dx computer. The crystallographic data, atomic coordinates and selected bond lengths and angles are given in Tables II and III.

Crystal data for $C_{27}H_{20}N_2O_2$; M = 404.45 Crystallises from toluene as colourless blocks; crystal dimensions $0.65 \times 0.35 \times 0.175$ mm. Triclinic, $a = 9.058(3)$, $b = 11.012(4)$, $c = 11.985(2)$ Å, $\alpha = 106.77(2)°$, $\beta = 107.59(3)°$ $\gamma = 97.948(3)°$, $U = 1057.1$ (5) $Å^3$, $Z = 2$, $D_c = 1.271$g cm^{-3}, space group $P\bar{1}$ (C_i^1, No. 2) MoK_α radiation ($\bar{\lambda} = 0.71073$ Å), $\mu(Mo\text{-}K_\alpha) = 0.081 mm^{-1}$, $F(000) = 424$.

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