

X-Ray Structural Studies of Stereoisomeric Bi(14*H*-dibenzo[4,5:6,7][1,3]-diazepino[2,1-*a*]isoindol-14-ylidene)s obtained from the Reaction of 2,2'-Diaminobiphenyl with *o*-Phthalaldehyde

D. Muriel Hall

Department of Chemistry, Royal Holloway and Bedford New College, Egham, Surrey, TW20 0EX

Hwang Huaun-Yong and Joan M. Insole*

Department of Physical Sciences, North East London Polytechnic, Romford Road, London E15 4LZ

Nigel P. C. Walker

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS

Reaction of 2,2'-diaminobiphenyl with *o*-phthalaldehyde yielded a number of products including two bi-(14*H*-dibenzo[4,5:6,7][1,3]diazepino[2,1-*a*]isoindol-14-ylidene)s, (**A**) and (**B**); each was converted on heating into a third isomer (**D**). The crystal structure of (**A**), and that of (**D**), as the solvated trifluoroacetate salt, were determined; (**A**), previously thought to be the *trans*-isomer, is in fact the *cis*-(*R,R*)/(*S,S*)-isomer (**1a**), a racemic compound, and (**D**) is the *meso trans*-(*R,S*)-isomer (**2b**). Compound (**B**) is considered to be the racemic *trans*-(*R,R*)/(*S,S*)-isomer (**2a**). The crystal structures of (**A**) and (**D**) and the ¹³C n.m.r. and u.v. spectra of all three isomers are discussed.

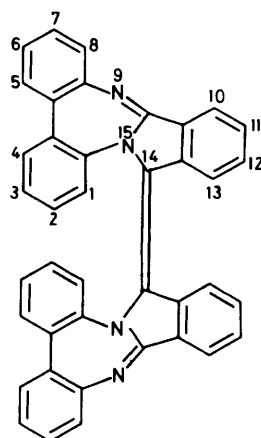
As part of an extended investigation¹⁻⁴ into 2,2'-bridged biphenyls with a heterocyclic bridging ring, we studied the interaction of 2,2'-diaminobiphenyl with *o*-phthalaldehyde. A previous attempt⁵ to study this reaction had given 'only red polymeric compounds,' which had not been identified.

The reaction is complex, and we had already isolated a number of products when Bindra and Elix⁶ reported that they had investigated this reaction and isolated four products, to which they assigned the structures (1)–(4) on the basis of spectroscopic evidence and chemical interconversion. Since our findings were not entirely in accord with theirs, we have made a further study of the reaction and report that the bi(isoindolinylidene) to which they assigned the *trans* structure (2) is shown by crystal structure determination to be a *cis*-isomer (**1a**); and the bi(isoindolinylidene) which was assigned the *cis* structure (1) by Bindra and Elix⁶ is most probably a *trans*-isomer (**2a**).

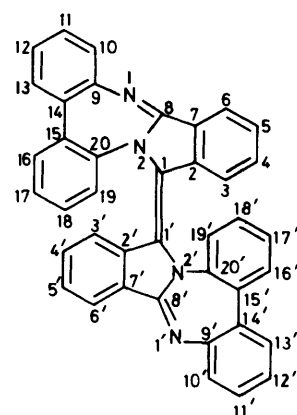
In the present work, equimolar quantities of 2,2'-diaminobiphenyl and *o*-phthalaldehyde were allowed to react in methanolic solutions at room temperature. Products were isolated by crystallisation and chromatographic techniques.

Products isolated included two bi(isoindolinylidene)s, C₄₀H₂₄N₄, (**A**), yield ≤18%, m.p. 270–272 °C, and (**B**) (0.4%), changing at 276–280 °C but not melting up to 360 °C; a substance (**C**), C₄₀H₂₆N₄O, m.p. 265–267 °C (≤13%); 2-amino-2'-phthalimidobiphenyl⁷ (**5**), m.p. 176–177 °C; and the dimer^{8,9} of *o*-phthalaldehyde, m.p. 177–178 °C (**6**). The yields and relative proportions of (**A**) and (**C**) depended upon the reaction time. If the reaction mixture was worked up and product isolated within a few days, more (**C**) than bi(isoindolinylidene), (**A**), was isolated, but the proportions were reversed if reaction time was prolonged. There were other unidentified products; some unchanged 2,2'-diaminobiphenyl was recovered.

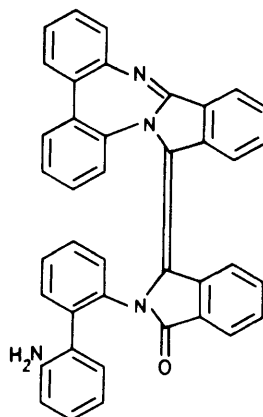
Substance (**C**) contains a carbonyl group and an amino group (i.r.) and is considered to be a mixture of the *cis*- and *trans*-amides, (**3**) and (**4**); the ¹³C n.m.r. spectrum shows at least 62 signals and the ¹H n.m.r. spectrum shows two singlets interchangeable with D₂O. Bindra and Elix isolated two compounds of this structure; to the one with m.p. 262 °C they assigned the *cis* configuration; the other, obtained in too small an amount to determine a m.p., they considered to be the *trans* compound.



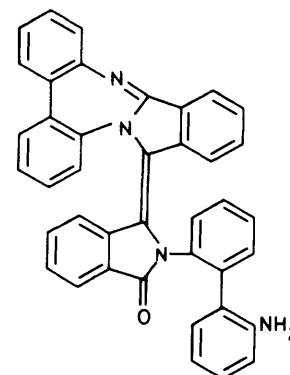
(1)* *cis*
(1a) *cis*-(*R,R*)/(*S,S*)
(1b) *cis*-(*R,S*)



(2)† *trans*
(2a) *trans*-(*R,R*)/(*S,S*)
(2b) *trans*-(*R,S*)

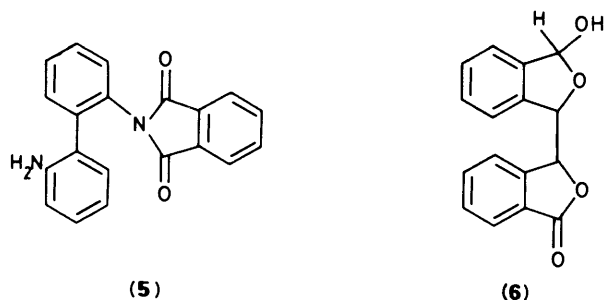


(3)



(4)

* Numbering for nomenclature. † Numbering for crystal structure and ¹³C n.m.r. data.



The two bi(isoindolinylidene)s obtained by Bindra and Elix had m.p. 267–268 and 276–280 °C; the *trans* and *cis* configurations respectively were assigned to them. Our compound (A) closely resembles their supposed *trans* compound, but our compound (B) differs from their supposed *cis* compound in that it undergoes a visible solid-phase change at *ca.* 275–280 °C but does not melt up to 360 °C, whereas their compound is reported to melt at 276–280 °C.

Further investigation showed that our compound (A) re-solidified, after melting, to a yellow compound not melting below 360 °C. Thermal analysis shows the change as an endothermic event immediately followed by an exothermic event. The product was identical with that obtained by heating (B) and is a third bi(isoindolinylidene), (D), which has not been previously reported. High-pressure liquid chromatography analysis of the entire original reaction product revealed the presence of (A) and (B), but no (D).

Since spectroscopic investigations (i.r., u.v., ^1H n.m.r., ^{13}C n.m.r.) failed to clarify the situation, the crystal structure of product (A) was determined.

Crystal Structures.—Suitable crystals of (A) were obtained from ethyl acetate. Compound (A) is a *cis*-bi(isoindolinylidene) (1a) in which the two biphenyl units are of the same con-

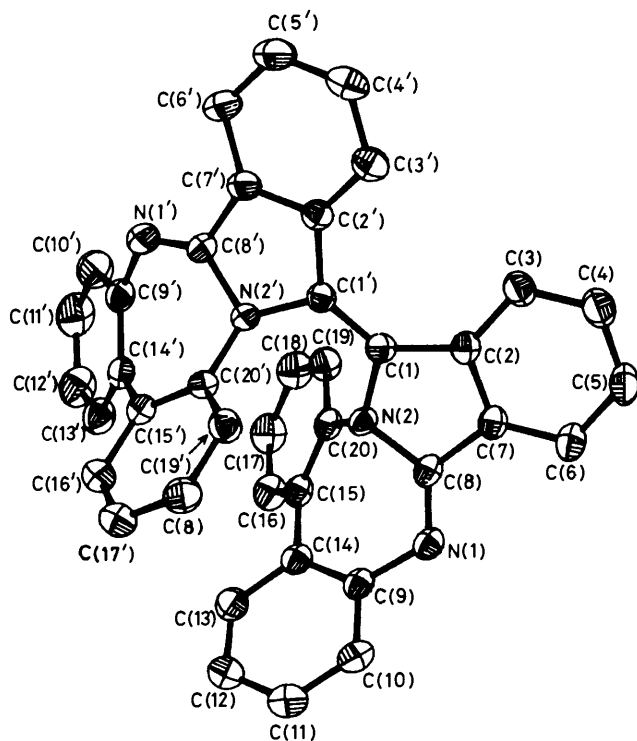


Figure 1. Thermal ellipsoid diagram of compound (1a) with crystallographic numbering scheme

Table 1. Selected bond lengths (Å) with e.s.d.s in parentheses (crystallographic numbering scheme)

	(1a) ^a	(2b) ^b
C(1)–C(2)	1.471(2); 1.469(3)	1.473(8)
C(1)–N(2)	1.432(2); 1.432(2)	1.449(7)
C(1)–C(1')	1.361(3)	1.325(10)
C(2)–C(3)	1.394(3); 1.390(3)	1.398(9)
C(2)–C(7)	1.403(3); 1.400(3)	1.405(8)
C(3)–C(4)	1.385(3); 1.388(3)	1.376(9)
C(4)–C(5)	1.388(3); 1.384(3)	1.392(10)
C(5)–C(6)	1.382(3); 1.382(3)	1.378(9)
C(6)–C(7)	1.387(3); 1.396(3)	1.385(8)
C(7)–C(8)	1.459(3); 1.456(3)	1.447(8)
C(8)–N(1)	1.285(2); 1.284(2)	1.298(7)
C(8)–N(2)	1.429(2); 1.423(2)	1.382(7)
N(1)–C(9)	1.413(2); 1.408(3)	1.441(8)
C(9)–C(10)	1.399(3); 1.393(3)	1.398(9)
C(9)–C(14)	1.409(3); 1.411(3)	1.377(9)
C(10)–C(11)	1.388(3); 1.373(4)	1.382(11)
C(11)–C(12)	1.377(3); 1.385(4)	1.368(12)
C(12)–C(13)	1.387(3); 1.371(3)	1.371(11)
C(13)–C(14)	1.400(3); 1.396(3)	1.401(9)
C(14)–C(15)	1.476(3); 1.478(3)	1.473(9)
C(15)–C(16)	1.399(3); 1.408(3)	1.393(9)
C(15)–C(20)	1.392(3); 1.396(3)	1.394(8)
C(16)–C(17)	1.383(3); 1.377(3)	1.374(10)
C(17)–C(18)	1.391(3); 1.377(3)	1.386(10)
C(18)–C(19)	1.380(3); 1.385(3)	1.377(9)
C(19)–C(20)	1.386(3); 1.380(3)	1.375(8)
C(20)–N(2)	1.444(2); 1.433(2)	1.453(7)

^a The first figure in this column refers to the C(1)–C(20) half of the molecule, the second figure to the C(1')–C(20') half. ^b Protonated at N(1) and N(1').

figuration, i.e. both (*R*) or both (*S*), and packing diagrams show that enantiomeric molecules alternate throughout the crystal. Selected bond lengths are given in Table 1, selected bond angles in Table 2, selected torsional angles in Table 3, and fractional atomic co-ordinates in Table 6. A thermal ellipsoid diagram of compound (1a) is shown in Figure 1.

Stereochemical considerations suggest that, for each geometrical arrangement with respect to the central double bond, the two biphenyl units could possess either the same chirality [(*R,R*) or (*S,S*), forming an enantiomeric pair], or opposite chirality [(*R,S*), a *meso* compound]; thus, there are potentially four diastereoisomeric products, two of which are racemates. Inspection of molecule models suggests, however, that in the *cis*-(*R,S*)-isomer (1b), the dibenzodiazepine systems would need to suffer severe distortion if an unacceptably large deviation from a planar configuration about the central carbon–carbon double bond were to be avoided. Nevertheless, even if structure (1b) could be discounted for compounds (B) and (D), it is still not possible on spectroscopic grounds to assign the two remaining structures, (2a) and (2b), individually to (B) and (D). Therefore the crystal structure of product (D) has also been determined.

Suitable crystals of compound (D) were obtained from an acetone–trifluoroacetic acid mixture and were stored in a sealed ampoule. Otherwise, they tended to lose solvent and become opaque. [Selected bond lengths, Table 1; selected bond angles, Table 2; selected torsional angles, Table 3; fractional atomic co-ordinates, Table 7; a thermal ellipsoid diagram, Figure 2]. Compound (D) is a *trans*-bi(isoindolinylidene), the biphenyl units being of opposite configuration; hence it has the achiral *meso* structure (2b). There are four molecules of $\text{CF}_3\text{CO}_2\text{H}$ associated with every molecule of (2b). The fluorine atoms of two of the $\text{CF}_3\text{CO}_2\text{H}$ molecules show partial occupation of positions, *ca.* two-thirds in one position and *ca.* one-third in

Table 2. Selected bond angles ($^{\circ}$) with e.s.d.s in parentheses (crystallographic numbering scheme)

	(1a) ^a	(2b) ^b
C(2)–C(1)–N(2)	106.6(1); 106.4(1)	106.2(5)
C(2)–C(1)–C(1')	134.4(2); 133.4(2)	131.8(4)
N(2)–C(1)–C(1')	118.7(2); 119.3(2)	121.8(5)
C(1)–C(2)–C(3)	133.4(2); 133.4(2)	132.5(5)
C(1)–C(2)–C(7)	107.8(2); 107.5(2)	107.8(5)
C(3)–C(2)–C(7)	118.7(2); 119.2(2)	119.7(6)
C(2)–C(3)–C(4)	118.8(2); 118.7(2)	117.4(7)
C(3)–C(4)–C(5)	121.6(2); 121.6(2)	122.8(7)
C(4)–C(5)–C(6)	120.6(2); 120.9(2)	120.3(7)
C(5)–C(6)–C(7)	117.9(2); 117.5(2)	117.9(6)
C(2)–C(7)–C(6)	122.3(2); 122.0(2)	121.9(6)
C(2)–C(7)–C(8)	108.8(2); 109.2(2)	106.9(5)
C(6)–C(7)–C(8)	128.9(2); 128.7(2)	131.1(5)
C(7)–C(8)–N(1)	126.2(2); 125.6(2)	127.0(6)
C(7)–C(8)–N(2)	106.5(2); 106.3(2)	110.2(5)
N(1)–C(8)–N(2)	127.1(2); 127.7(2)	122.8(6)
C(8)–N(1)–C(9)	120.0(2); 121.6(2)	124.6(6)
N(1)–C(9)–C(10)	114.4(2); 114.9(2)	116.0(7)
N(1)–C(9)–C(14)	126.2(2); 126.3(2)	121.9(6)
C(10)–C(9)–C(14)	119.4(2); 118.7(2)	122.1(7)
C(9)–C(10)–C(11)	121.0(2); 121.8(2)	118.7(8)
C(10)–C(11)–C(12)	119.5(2); 119.5(2)	119.9(8)
C(11)–C(12)–C(13)	120.5(2); 119.6(2)	121.1(8)
C(12)–C(13)–C(14)	121.0(2); 122.2(2)	120.8(8)
C(9)–C(14)–C(13)	118.5(2); 118.1(2)	117.3(7)
C(9)–C(14)–C(15)	122.7(2); 122.7(2)	123.1(6)
C(13)–C(14)–C(15)	118.8(2); 119.2(2)	119.6(7)
C(14)–C(15)–C(16)	119.6(2); 119.2(2)	120.3(6)
C(14)–C(15)–C(20)	122.5(2); 123.5(2)	122.7(6)
C(16)–C(15)–C(20)	117.9(2); 117.3(2)	116.9(6)
C(15)–C(16)–C(17)	121.5(2); 121.8(2)	122.0(7)
C(16)–C(17)–C(18)	119.1(2); 119.5(2)	119.6(7)
C(17)–C(18)–C(19)	120.6(2); 120.1(2)	119.7(7)
C(18)–C(19)–C(20)	119.7(2); 120.5(2)	120.1(7)
C(15)–C(20)–C(19)	121.2(2); 120.8(2)	121.7(6)
C(15)–C(20)–N(2)	117.9(2); 118.9(2)	118.4(6)
C(19)–C(20)–N(2)	120.9(2); 120.3(2)	120.0(6)
C(1)–N(2)–C(8)	108.6(1); 108.7(1)	107.1(5)
C(1)–N(2)–C(20)	120.2(1); 122.1(1)	119.6(5)
C(8)–N(2)–C(20)	115.2(1); 117.0(1)	115.1(5)

^{a,b} See Table 1.

another. Only two of the four acidic protons could be located, protonating the two sp^2 -hybridised nitrogen atoms, N(1). A molecular packing diagram of compound (2b) is shown in Figure 3. All hydrogen atoms and the minor sites of the fluorine atoms in 50% of the CF_3CO_2H molecules are omitted. The view is down the *a*-axis.

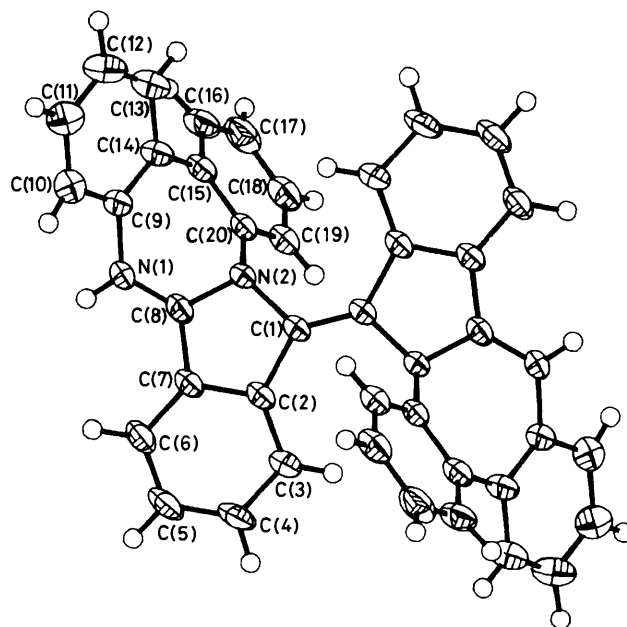
We consider therefore that the remaining bi(isoindolinyl)idene (B) is the other *trans*-isomer (2a).

There is molecular overcrowding in the *cis*-isomer (1a), where the biphenyl units partially overlap one another. This leads to some distortion in the region of the C(1)–C(1') double bond, as shown by the C(2)–C(1)–C(1')–C(2') torsional angle of 10.8° and the C(1)–C(1') bond length of 1.361 Å. In (2b) the corresponding torsion angle is the expected 180.0°, and the bond length a somewhat shorter 1.325 Å. This distortion does not extend to the biphenyl units themselves, for there are only slight differences in the torsion angles, C(9)–C(14)–C(15)–C(20) and C(13)–C(14)–C(15)–C(16), of (1a) and (2b).

The other region in which substantial differences between the two structures (1a) and (2b) occur is centred round the N(1) atom, which is protonated in (2b). If the N(1)=C(8)–N(2) system is regarded as an amidine, then protonation may be expected to occur at N(1), the resultant positive charge being delocalised

Table 3. Selected torsional angles ($^{\circ}$) (crystallographic numbering scheme)

	(1a) ^a	(2b) ^b
C(2)–C(1)–C(1')–C(2')	10.8	180.0
C(7)–C(8)–N(1)–C(9)	166.1; 164.5	–163.5
C(8)–N(1)–C(9)–C(14)	39.4; 37.1	–45.1
N(1)–C(9)–C(14)–C(15)	4.8; 5.4	–5.4
C(9)–C(14)–C(15)–C(20)	–43.5; –41.5	42.8
C(14)–C(15)–C(20)–N(2)	3.5; 3.3	–1.2
C(15)–C(20)–N(2)–C(8)	61.0; 57.6	–64.3
C(20)–N(2)–C(8)–N(1)	–60.5; –56.0	56.8
N(2)–C(8)–N(1)–C(9)	–7.5; –8.5	15.6
C(1)–N(2)–C(20)–C(15)	–166.1; –164.4	165.9
C(7)–C(8)–N(2)–C(1)	–13.2; –13.3	11.6
C(8)–N(2)–C(1)–C(2)	12.6; 14.0	–13.5
C(1)–C(2)–C(7)–C(8)	–1.0; 1.1	–3.7
C(13)–C(14)–C(15)–C(16)	–40.4; –36.2	40.6

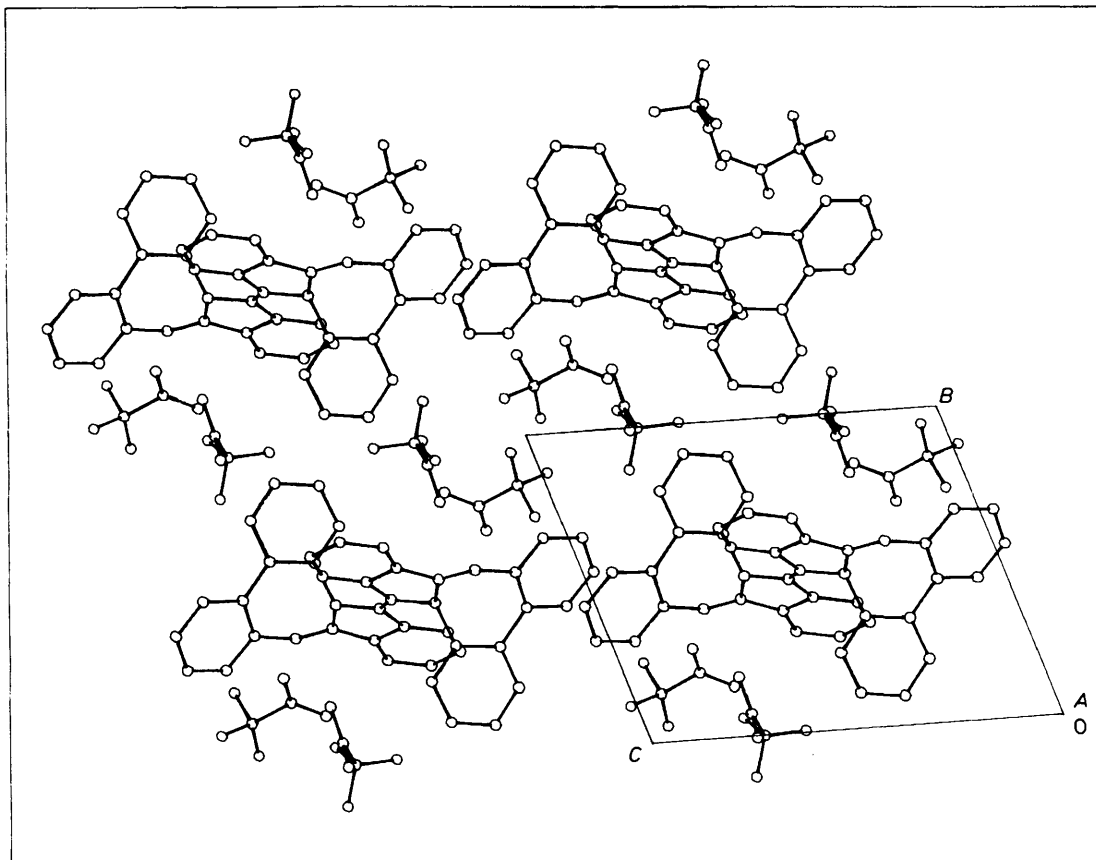
^{a,b} See Table 1.**Figure 2.** Thermal ellipsoid diagram of compound (2b) with crystallographic numbering scheme

between N(1) and N(2). The N(1)–C(9) single and C(8)=N(1) double bonds are longer in (2b) than in (1a), whereas the C(8)–N(2) and C(9)–C(14) bonds are shorter. The bond angles C(8)–N(1)–C(9), C(7)–C(8)–N(2), and C(10)–C(9)–C(14) are larger in (2b) than in (1a); N(1)–C(9)–C(14) and N(1)–C(8)–N(2) are smaller. The largest differences (in magnitude) in torsional angles, after that mentioned above in connection with the central C=C double bond, are shown by C(8)–N(1)–C(9)–C(14) and N(2)–C(8)–N(1)–C(9), which are both larger in (2b). These differences suggest diminishing conjugation of the C(8)=N(1) π electrons with the biphenyl system accompanied by increasing conjugation of these C(8)=N(1) π electrons with the lone pair on N(2) in (2b). U.v. spectroscopy supports this suggestion.

U.v. Spectroscopy.—The u.v. spectra of products (1a), (2a), and (2b) are summarised in Table 4. The spectrum of non-protonated (2b) (*i.e.*, not recrystallised) shows three maxima, at 250, 314, and 450 nm. In the spectrum of the trifluoroacetic acid–acetone-recrystallised compound (2b), the short-wave (bi-

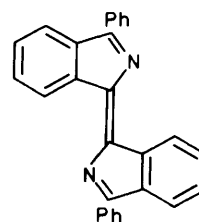
Table 4. Electronic spectra of the bi(isoindolinylidene)s in dichloromethane (wavelengths in parentheses denote inflections)

(1a)		(2a)		(2b)		(2b) - H ⁺	
$\lambda_{\max.}$	$\epsilon_{\max.}$	$\lambda_{\max.}$	$\epsilon_{\max.}$	$\lambda_{\max.}$	$\epsilon_{\max.}$	$\lambda_{\max.}$	$\epsilon_{\max.}$
250	58 300	249	76 390	250	60 700	242	50 800
(302)	20 600						
		318	24 300	314	19 900	350	11 500
(332)	17 200						
384	11 200	454	16 510	450	12 700	534	11 900
476	14 600						

**Figure 3.** Molecular packing diagram of compound (2b)

phenyl) maximum has undergone a slight hypsochromic shift (242 nm) and the other maxima show large bathochromic shifts to 350 and 534 nm. Indeed, if $\text{CF}_3\text{CO}_2\text{H}$ is added to a solution of non-recrystallised (2b), these shifts are seen to occur, and when opaque crystals of (2b) are used a spectrum intermediate between those given in Table 4 is obtained. That protonation of such a heterocyclic system may lead to enhanced conjugation is illustrated by 3,3'-diphenyl bi-(1*H*-isoindol-1-ylidene) (7), where the absorption band at 447 nm (in EtOH) undergoes a bathochromic shift to 462 nm on addition of hydrochloric acid.¹⁰

The differences between the u.v. spectra of (1a) and non-protonated (2b) may be due to the previously mentioned distortion introduced into the *cis*-isomer (1a) by molecular overcrowding. This distortion appears to have a minimal effect on the biphenyl dihedral angle, and the biphenyl absorption band at 250 nm is the one feature which the spectra of these isomers have in common. However, such distortion would be expected to lead to diminished conjugation elsewhere in the

**(7)**

molecule, and yet the long-wave band occurs at a longer wavelength in (1a) (476 nm) than in (2b) (450 nm).

The u.v. spectrum of the remaining bi(isoindolinylidene) (B) supports our contention that it has the *trans*-(*R,R*)/(*S,S*) structure (2a), for, with maxima at 249, 318, and 454 nm, it shows only minor differences from the spectrum of non-protonated *trans*-(*R,S*) (2b).

Table 5. ^{13}C N.m.r. spectra (p.p.m. from SiMe_4) in CDCl_3 (crystallographic numbering)

Assignments	(1a)	(2a)	(2b) ^a
C(8)	161.78 ^b	162.50 ^b	162.64 ^b
C(9)	147.96 ^b	147.97 ^b	147.51 ^b
C(20)	143.16 ^b	147.55 ^b	146.35 ^b
C(7)	136.42 ^b	136.55 ^b	137.94 ^b
	134.11 ^b	133.70 ^b	133.70 ^b
	134.11 ^b	132.11 ^b	132.77 ^b
	131.98 ^b	131.78 ^b	131.47 ^b
	131.32	131.97	131.17
	129.61	131.87	130.72
	129.34	129.00	129.12
	128.99	128.93	128.99
	127.63	128.81	128.79
	127.56	128.69	128.57
	126.98	127.79	127.53
	125.30	125.93	125.84
	124.90	125.93	125.74
	123.99 ^b	127.79 ^b	127.85 ^b
	123.50	125.29	125.47
C(10)	122.43	122.74	122.64
C(19)	121.59	119.00	118.32

^a Non-protonated (2b). ^b Signal attributable to a quaternary carbon atom.

^{13}C N.m.r. Spectroscopy.—The ^{13}C n.m.r. assignments (Table 5) were made on the basis of a study of literature data and by inspection of the ORTEP diagrams (Figures 1 and 2) and of molecular models of compounds (1a), (2a), and (2b).

In each compound, (1a), (2a), and (2b), the only unambiguous assignment is that of C(8), an sp^2 -hybridised carbon atom, deshielded by attachment to two nitrogen atoms. The next two most highly deshielded atoms are C(9) and C(20), each bonded to one nitrogen atom. However, C(9) is bonded to an sp^2 -hybridised nitrogen atom and should be more highly deshielded than C(20). On the other hand, in (1a), C(20) should experience shielding due to the overlap of the innermost biphenyl rings. Thus, the signals at δ_c 147.96 (1a), 147.97 (2a), and 147.51 (2b) have been assigned to C(9) and at 143.16 (1a), 147.55 (2a), and 146.35 (2b) to C(20). C(7) is also deshielded by the C=N bond and is assigned the signal with the fourth highest chemical shift.

The most highly shielded tertiary carbon atoms are C(10) and C(19), *ortho* to the highly deshielded, nitrogen-bonded C(9) and C(20) atoms. These are the only two tertiary carbon atoms to which assignments may be made with some certainty. Accepted shielding/deshielding influences of substituents on aromatic carbon atoms cannot be rigidly applied in the case of *ortho*-disubstituted benzenes.¹¹ Other shielding/deshielding influences may, of course, be identified. One such is the already mentioned mutual shielding of the innermost biphenyl rings in (1a). Also, in (1a), the C(3), C(3') carbons of the two phthalyl rings come sufficiently close together to deshield one another [H(3) and H(3') are only 1.811 Å apart], while in (2b) the phthalyl ring makes an oblique mutually shielding approach to the innermost biphenyl ring of the other half of the molecule, coming closest to C(19'). However, the balance of these influences is not sufficiently clear-cut for satisfactory assignments to be made to the other carbon atoms.

Experimental

I.r. spectra were determined for KBr discs on a Perkin-Elmer 377 grating spectrophotometer or on a Perkin-Elmer Infracord spectrophotometer. U.v. spectra were determined in dichloro-methane on a Pye Unicam SP 8-100 spectrophotometer.

Table 6. Fractional atomic co-ordinates ($\times 10^4$) for compound (1a) (crystallographic numbering scheme)

	x	y	z
C(1)	4 689(1)	676(2)	1 752(2)
C(2)	5 240(1)	831(2)	1 419(2)
C(3)	5 631(1)	227(2)	1 076(2)
C(4)	6 130(1)	603(2)	849(2)
C(5)	6 247(1)	1 563(2)	951(2)
C(6)	5 867(1)	2 174(2)	1 295(2)
C(7)	5 371(1)	1 794(2)	1 538(2)
C(8)	4 909(1)	2 272(2)	1 929(2)
N(1)	4 839(1)	3 177(2)	1 988(1)
C(9)	4 325(1)	3 545(2)	2 213(2)
C(10)	4 175(1)	4 371(2)	1 780(2)
C(11)	3 666(1)	4 777(2)	1 891(2)
C(12)	3 311(1)	4 383(2)	2 462(2)
C(13)	3 461(1)	3 594(2)	2 931(2)
C(14)	3 968(1)	3 161(2)	2 817(2)
C(15)	4 114(1)	2 339(2)	3 349(2)
C(16)	3 978(1)	2 346(2)	4 202(2)
C(17)	4 084(1)	1 573(2)	4 715(2)
C(18)	4 331(1)	772(2)	4 373(2)
C(19)	4 481(1)	754(2)	3 538(2)
C(20)	4 375(1)	1 536(2)	3 033(2)
N(2)	4 533(1)	1 543(1)	2 159(1)
C(1')	4 318(1)	-39(2)	1 688(2)
C(2')	4 343(1)	-1 017(2)	1 362(2)
C(3')	4 689(1)	-1 478(2)	804(2)
C(4')	4 600(1)	-2 434(2)	632(2)
C(5')	4 183(1)	-2 936(2)	1 014(2)
C(6')	3 828(1)	-2 491(2)	1 559(2)
C(7')	3 908(1)	-1 521(2)	1 712(2)
C(8')	3 593(1)	-885(2)	2 246(2)
N(1')	3 229(1)	-1 143(2)	2 777(2)
C(9')	3 039(1)	-519(2)	3 404(2)
C(10')	2 925(1)	-949(2)	4 172(2)
C(11')	2 757(1)	-430(2)	4 855(2)
C(12')	2 684(1)	544(2)	4 779(2)
C(13')	2 776(1)	977(2)	4 020(2)
C(14')	2 953(1)	470(2)	3 318(2)
C(15')	3 011(1)	972(2)	2 508(2)
C(16')	2 636(1)	1 691(2)	2 295(2)
C(17')	2 689(1)	2 222(2)	1 573(2)
C(18')	3 112(1)	2 036(2)	1 030(2)
C(19')	3 478(1)	1 313(2)	1 209(2)
C(20')	3 430(1)	789(2)	1 938(2)
N(2')	3 810(1)	44(1)	2 120(1)

Molecular masses were determined by the P.C.M.U., Harwell. ^1H N.m.r. spectra were determined for CDCl_3 solutions, with SiMe_4 as internal standard, by the P.C.M.U., Harwell (100 or 220 MHz). ^{13}C N.m.r. spectra were determined for CDCl_3 solutions, with SiMe_4 as internal standard, by the P.C.M.U., Harwell, and under the U.L.I.R.S. scheme at Queen Mary College and King's College, University of London. M.p.s were measured on a Kofler apparatus and are uncorrected.

X-Ray Crystallography.—Unit-cell dimensions and intensity data for compounds (1a) and (2b) were obtained using an Enraf-Nonius CAD4 diffractometer and Ni-filtered $\text{Cu-K}\alpha$ (λ 1.541 78 Å) radiation and $\omega/2\theta$ scans, following procedures previously described in detail.¹²

Crystal data: (1a), $\text{C}_{40}\text{H}_{24}\text{N}_4$, $M = 560.66$, orthorhombic, $a = 24.600(3)$, $b = 14.039(1)$, $c = 15.931(2)$ Å, $V = 5 502(2)$ Å³, space group $Pbca$, $Z = 8$, $D_c = 1.354$ g cm⁻³, $F(000) = 2 336$, $\mu(\text{Cu-K}\alpha) = 5.88$ cm⁻¹. 5 787 Unique reflections measured, $3 \leq \theta \leq 70^\circ$, 4 520 observed [$I > 3\sigma(I)$].

For (2b), $[\text{C}_{40}\text{H}_{24}\text{N}_4][\text{CF}_3\text{CO}_2\text{H}]_4$, $M = 1 016.76$, triclinic, $a = 8.774(1)$, $b = 11.040(2)$, $c = 13.072(1)$ Å, $\alpha =$

Table 7. Fractional atomic co-ordinates ($\times 10^4$) for compound (**2b**) (crystallographic numbering scheme)

	x	y	z
N(1)	3 559(6)	5 879(5)	2 535(4)
N(2)	1 640(5)	4 918(4)	3 809(3)
C(1)	707(6)	5 131(5)	4 822(4)
C(2)	1 589(6)	5 748(5)	5 229(4)
C(3)	1 406(7)	6 018(6)	6 222(5)
C(4)	2 426(8)	6 659(7)	6 322(5)
C(5)	3 588(8)	7 055(7)	5 479(6)
C(6)	3 782(7)	6 787(6)	4 500(5)
C(7)	2 794(6)	6 115(5)	4 391(4)
C(8)	2 739(6)	5 652(5)	3 501(4)
C(9)	3 171(7)	5 704(6)	1 591(4)
C(10)	3 260(8)	6 735(7)	589(5)
C(11)	2 851(9)	6 648(9)	-341(6)
C(12)	2 423(10)	5 545(9)	-274(6)
C(13)	2 380(9)	4 520(8)	706(5)
C(14)	2 790(7)	4 567(6)	1 666(5)
C(15)	2 885(7)	3 392(6)	2 681(5)
C(16)	3 586(8)	2 060(6)	2 632(6)
C(17)	3 683(8)	940(6)	3 560(6)
C(18)	3 092(8)	1 125(6)	4 582(6)
C(19)	2 428(7)	2 430(6)	4 659(5)
C(20)	2 320(6)	3 543(5)	3 723(4)
C(32)	3 446(10)	2 114(9)	8 190(7)
O(31)	3 488(11)	1 608(11)	7 496(5)
O(32)	4 125(7)	2 889(6)	8 126(5)
C(41)	-573(9)	-8(8)	7 273(6)
C(42)	569(11)	709(10)	7 366(6)
O(41)	21(8)	1 888(6)	7 299(6)
O(42)	2 024(7)	-65(6)	7 467(5)
F(41)	-2 112(6)	587(5)	7 586(5)
F(42)	-234(7)	-1 310(5)	7 875(5)
F(43)	-525(8)	63(7)	6 248(4)
C(31)	2 579(12)	1 550(10)	9 315(8)
F(31A) ^a	3 529(10)	1 223(9)	10 148(7)
F(32A)	2 105(11)	511(9)	9 471(7)
F(33A)	1 196(10)	2 563(8)	9 424(6)
F(31B)	3 297(21)	20(16)	9 447(13)
F(32B)	1 139(20)	1 470(18)	9 340(13)
F(33B)	2 751(21)	1 810(17)	10 078(14)

^a A and B fluorine sites are the two components of the CF₃ rotational disorder. The occupancies of the two sites are 0.6667 (A) and 0.3333 (B).

68.73(1), $\beta = 77.60(1)$, $\gamma = 68.75(1)^\circ$, $V = 1 095(1) \text{ \AA}^3$, space group $P\bar{1}$, $Z = 1$, $D_c = 1.54 \text{ g cm}^{-3}$, $F(000) = 512$, $\mu(\text{Cu-K}\alpha) = 11.1 \text{ cm}^{-1}$, 4 322 Data measured, $3 \leq \theta \leq 70^\circ$, and 2 813 observed [$I > 3\sigma(I)$].

Both structures were solved by direct methods and refined by least squares. All non-hydrogen atoms were assigned anisotropic thermal parameters except for the atoms of the CF₃ group in one of the independent trifluoroacetic acid units, in which the fluorines were disordered over two sites. These atoms and all hydrogens were refined with isotropic thermal parameters. The final R -values were 0.050 (**1a**) and 0.097 (**2b**). Final fractional atomic co-ordinates are given in Tables 6 (**1a**) and 7 (**2b**). Calculations for the structure determination of compound (**1a**) were made using programs of the Enraf-Nonius SDP Package on a PDP 11/34 computer, whilst for (**2b**) the SHELX program was used on a VAX 11/750 computer.*

* Supplementary data [see section 5.6.3 of Instructions for Authors (1987), in the January issue]. Tables of anisotropic temperature factors and hydrogen fractional atomic co-ordinates and isotropic temperature factors have been deposited at the Cambridge Crystallographic Data Centre.

Reaction of 2,2'-Diaminobiphenyl with *o*-Phthalaldehyde.—(Method 1). A solution of 2,2'-diaminobiphenyl (11.04 g) in methanol was added to a solution of *o*-phthalaldehyde (8.04 g) in methanol (2 l in all). The mixture was left at room temperature for 1–2 months, then concentrated (to 1.3 l) and kept until crystals (3.2 g) were obtained. Recrystallisation of these from ethyl acetate gave orange-red prisms of the *cis*-*bi*(isoindolinylidene) (**1a**) (3.1 g), m.p. 270–272 °C (lit.,⁶ 267–268 °C) (Found: M^+ , 560.2000; C, 85.6; H, 4.2; N, 10.15%. $\text{C}_{40}\text{H}_{24}\text{N}_4$ requires M , 560.2001; C, 85.7; H, 4.3; N, 10.0%); ν_{max} . 1 640 cm^{-1} (C=N); δ_{H} 6.43–6.54 (4 H, m), 6.63–6.72 (2 H, m), 6.97–7.22 (10 H, m), 7.48 (2 H, t, J 7.5 Hz), 7.62 (2 H, t, J 7.5 Hz), 8.04 (2 H, d, J 7.5 Hz), and 8.49 (2 H, d, J 7.5 Hz); t.l.c. R_F 0.52 (silica; benzene).

Further concentration of the reaction mixture produced red crystals (3.97 g), which on recrystallisation from ethyl acetate gave the amides as a mixture of stereoisomers [probably (**3**) and (**4**)] (2.23 g), m.p. 265–267 °C (Found: M^+ , 578.2096; C, 82.9; H, 4.55; N, 9.8%. Calc. for $\text{C}_{40}\text{H}_{26}\text{N}_4\text{O}$: M , 578.2106; C, 83.0; H, 4.5; N, 9.7%; ν_{max} . 3 500 (NH₂), 3 400 (NH₂), 1 695 (CO), and 1 640 cm^{-1} (C=N); δ_{H} 2.80 and 3.17 (2 s, exchangeable with D₂O) and 5.63–8.35 (complex multiplet).

(Method 2). A solution of 2,2'-diaminobiphenyl (11.04 g) in methanol was added to a solution of *o*-phthalaldehyde (8.04 g) in methanol (2 l in all). The mixture was left at room temperature for 1–3 days, then concentrated to give a product (3.08 g), which on fractional crystallisation from ethyl acetate gave the amides (**3**) and (**4**) (1.49 g), m.p. 265–267 °C, and *cis*-*bi*(isoindolinylidene) (**1a**) (0.69 g), m.p. 270–272 °C.

The original mother liquor was evaporated to dryness and the residue was chromatographed on silica gel with benzene, ether, light petroleum (b.p. 40–60 °C), and dichloromethane as eluants. Several products were obtained, including (a) an orange-red *trans*-*bi*(isoindolinylidene), (**2a**) (67 mg, from ethanol), changing to yellow at ca. 275–280 °C and not melting below 360 °C (Found: M^+ , 560.2000; C, 86.2; H, 4.1; N, 9.6%. $\text{C}_{40}\text{H}_{24}\text{N}_4$ requires M , 560.2001; C, 85.7; H, 4.3; N, 10.0%); ν_{max} . 1 640 cm^{-1} (C=N); R_F 0.65 (silica; benzene); (b) 2-amino-2'-phthalimidobiphenyl (**5**) (1.3 g, from ethyl acetate), m.p. 176–177 °C (lit.,⁷ 176–177 °C), mixed m.p. with authentic sample, 176–177 °C; and (c) 1,3'-dihydro-3'-hydroxy-1,1'-*bi*-isobenzofuran-3(1*H*)-one (**6**) (63 mg, from benzene), m.p. 177–178 °C (lit.,⁸ 184 °C), identical (mixed m.p., i.r.) with an authentic sample.

Conversion of (1a**) into (**2b**).**—Racemic *cis*-*bi*(isoindolinylidene) (**1a**) (orange-red) was heated until it melted, whereupon (272–274 °C) it resolidified (yellow) and remained unchanged at 320 °C for 30 min. The product was *meso*-*trans*-*bi*(isoindolinylidene) (**2b**), no melting below 360 °C (Found: C, 85.8; H, 4.2; N, 9.9. $\text{C}_{40}\text{H}_{24}\text{N}_4$ requires C, 85.7; H, 4.3; N, 10.0%); ν_{max} . 1 650 cm^{-1} (C=N); R_F 0.72 (silica; benzene).

Conversion of (2a**) into (**2b**).**—A few crystals (orange-red) of racemic *trans*-*bi*(isoindolinylidene) (**2a**) were heated gradually to 320 °C and were kept at this temperature for 30 min. The crystals became opaque at ca. 80 °C and yellow at 276–280 °C. The product was (**2b**), identical (i.r., t.l.c.) with that obtained similarly from *cis*-compound (**1a**).

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References

- 1 S. R. Ahmed and D. M. Hall, *J. Chem. Soc.*, 1958, 3043; 1959, 3383; 1960, 4165.
- 2 D. M. Hall and J. M. Insole, *J. Chem. Soc.*, 1964, 2326.
- 3 D. M. Hall, H. Y. Hwang, and B. Bhanthumnavin, *J. Chem. Soc., Perkin Trans. 2*, 1973, 2131.
- 4 B. A. Behnam and D. M. Hall, *J. Chem. Soc., Perkin Trans. 1*, 1980, 107; *Org. Mass. Spectrom.*, 1980, **15**, 526; 1981, **16**, 123.
- 5 A. E. Blood and C. R. Noller, *J. Org. Chem.*, 1957, **22**, 873.
- 6 A. P. Bindra and J. A. Elix, *Tetrahedron*, 1969, **25**, 5465.
- 7 S. Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, 1932, **6**, 307 (*Chem. Abstr.*, 1932, **26**, 3248).
- 8 A. Schonberg and A. Mustafa, *J. Am. Chem. Soc.*, 1955, **77**, 5755.
- 9 K. F. Cohen, J. T. Pinhey, and R. J. Smith, *Tetrahedron Lett.*, 1968, 4729.
- 10 R. Bonnett, S. A. North, R. F. Newton, and D. I. C. Stokes, *Tetrahedron*, 1983, **39**, 1401.
- 11 J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972; F. W. Wehrli and T. Wirthlin, 'Interpretation of Carbon-13 N.M.R. Spectra,' Heyden, London-New York-Rheine, 1980.
- 12 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

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